ST. LAWRENCE CEMENT, INC.
MISSISSAUGA - ONTARIO.

CONTRACT SERIAL NUMBER 1SQ79-00156
CONTRACTOR: ALLIED CHEMICAL CDA. LTD.
DSS REQUISITION NUMBER 23440-9-9056

ST. LAWRENCE CEMENT, INC., MISSISSAUGA, TEST PROGRAM WITH ALLIED CHEMICAL GYPSUM BYPRODUCT

SUMMARY

At Allied Chemical, Amherstburg, Ontario, hydrogen fluoride is produced by combining calcium fluoride with sulphuric acid. This process results in a calcium sulphate byproduct being generated. In 1978 and 1979, investigations began at St. Lawrence Cement, Mississauga, to study the viability of using this waste byproduct as a source of gypsum in the manufacture of Portland cement. Positive indications for the use of this material were observed in the initial work but inherent impurities made handling impossible. Through research studies performed at the Ontario Research Foundation, a method was developed to remove a major portion of the impurities.

Beginning in October, 1982, a two-phase test program using the modified gypsum byproduct was carried out. The second phase of the program was completed by September, 1983. Results of the program have shown that the cement produced with the Allied Chemical gypsum met all the required specifications. No abnormal variations in the chemical and physical characteristics of the finished cement were observed while using this gypsum. In addition, no unusual handling

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SUMMARY (CONT'D.)

problems with the gypsum byproduct were encountered throughout the test program.

INTRODUCTION

In general, to produce Portland cement, clinker with approximately 5% gypsum are interground in normally a ball mill to a desired fineness. The gypsum is added to regulate the setting time and early strength development of the cement paste. To a lesser extent, the gypsum also controls the shrinkage of the cement paste during curing. To produce the clinker, a chemically controlled ground mixture of limestone with lesser amounts of other additives such as shale or silica sand and iron are burnt in a kiln to a temperature of 1450°C.

At St. Lawrence Cement, Inc., Mississauga, three kilns are available for clinker production. One is a 4500 tonne per day dual four stage preheater-precalciner dry process kiln. The other two are identical 900 tonne per day wet process kilns. Utilizing the three kilns and the associated cement grinding mills, the plant has a rated production capacity of 2 million tonnes of Portland cement per year. At the rated capacity approximately 120 000 tonnes of gypsum would be required per annum.

One aspect for any industry, whether large or small, to be successful is that they are efficient in both operations and costs. Due to the aforementioned and also to environmental concerns, the use of byproducts that were at one time considered waste are now being utilized for various end uses.

INTRODUCTION (CONT'D.)

With this in mind, St. Lawrence Cement, Mississauga and Allied Chemical began investigating the possibility of using the gypsum byproduct of Allied Chemical as an additive for Portland cement manufacture.

In 1978 and 1979, Portland cement test grinds using the gypsum byproduct were performed at Mississauga. The initial indications were that this material could be a viable gypsum source for use in Portland cement manufacture. However, due to impurities, handling problems developed especially during periods of freeze-thaw conditions. From studies performed at the Ontario Research Foundation, a method was developed to remove the major portion of these impurities.

To assess the viability of using the modified Allied Chemical gypsum byproduct, 1230 tonnes of the material was received at St. Lawrence Cement, Mississauga, in October, 1982, for testing purposes.

The test program that was carried out would serve three purposes. First it was important to determine if the cement produced with the gypsum byproduct would meet the required specifications. Second, to investigate if unusual variations to the chemical and physical characteristics of the finished cement would result through the use of this gypsum byproduct. Third, to examine if short and longer term stockpiling would effect the chemical and physical characteristics of the gypsum byproduct.

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TEST PROGRAM

The test program at Mississauga was carried out in two phases. On December 15, 1982, the first phase of the program began with a 24 hour production test grind of Type 10 cement using the Allied Chemical gypsum. Simultaneously on an identical mill, Type 10 cement was produced using natural gypsum. During the grinding, Blaine fineness checks and %SO_3 determinations using X-Ray Fluorescence were performed every hour on each mill. A portion of the hourly samples were retained. Upon completion of the grinding, separate cement composite samples were prepared by blending the individual hourly samples. Each composite was then tested according to Canadian Standards Association (CSA) and American Society for Testing Materials (ASTM) specifications. In addition, laboratory concrete mixes were prepared from each of the cement composites.

For the second phase of the test program, the remaining Allied Chemical gypsum was stockpiled outside on the plant property and then on July 19, 1983 was again used in a 24 hour production test grind of Type 10 cement. Similar to the first phase, a simultaneous grind using natural gypsum was also carried out. The controlling and testing were identical to that of the first phase. Samples of the gypsum feeding each mill were taken during the grinding and also were tested.

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TEST RESULTS AND DISCUSSIONS

The results for Phase #1 of the program, are shown in Tables 1, 2 and 3. Chemically, the differences between the Type 10 cement ground with Allied Chemical gypsum and that produced with natural gypsum were minimal. The variations that did exist were those typically encountered under normal operation. One interesting comparison that could be made was with the "% insoluble residue" results. The considerably lower results obtained with the Allied Chemical gypsum indicates it is a purer form of gypsum. Similar to the chemical results, the comparison of physical results agreed very well for all parameters. The slight differences that did exist were those expected for normal operation. Keeping in line with the aforementioned comparisons, the concrete results agreed very well. The slightly higher penetration setting times observed in the concrete made from the cement produced with Allied Chemical gypsum are not considered significant as they are within the ASTM interlaboratory standard deviation for this test method. Although cannot be explained and by no means detrimental were the higher compressive strengths achieved in the concrete prepared from the cement which was ground with the Allied Chemical gypsum.

The Type 10 cement comparisons for Phase #2 of the test program are shown in Tables 4, 5 and 6. Generally, the comparisons were very similar to those observed in Phase #1. Chemically, only slight variations existed and again could be attributed to those expected under typical operation.

TEST RESULTS AND DISCUSSIONS (CONT'D.)

In comparing the physical results, increases in the air content and setting time were observed in the cement produced with the Allied Chemical gypsum. All other parameters agreed very well. Because of the higher air content in the mortar testing, air content comparisons were also performed in the concrete testing. As shown, there was no significant increases when comparing the concrete mixes. In addition the longer mortar setting time observed with the Type 10 cement produced with the Allied Chemical gypsum had no effect when the same cement was used in concrete.

No apparent effects were encountered in the Allied Chemical gypsum due to weathering. The gypsum maintained its coarse rock appearance in the stockpile after outside winter storage. Prior to use in the July 1983 grind, no unusual difficulties in handling and crushing were encountered. The comparison analysis for the Allied Chemical and natural gypsums are shown in Table #7. The Allied Chemical gypsum was higher in total %$CaSO_4$ than the natural gypsum and as indicated also contains a greater quantity of anhydrite gypsum. This is particularly beneficial for counteracting false set (early stiffening) characteristics of cement which occassionally occurs due to excessive milling temperatures. The purity of the Allied Chemical gypsum first mentioned in the Phase #1 results are again shown by the lower % insoluble results.

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CONCLUSIONS

Based on the results of this test program, the viability of using the Allied Chemical gypsum for Portland cement manufacture has been shown. At no time during the testing were detrimental effects encountered in the finished cement through the use of this material. The handling problems that were observed in the 1978 and 1979 testing of the gypsum byproduct were not encountered during this test program.

L. Zimmerman
Chief Chemist

CHEMICAL RESULTS

TEST #1

1982 12 15

TYPE 10 CEMENT

% COMPOSITION	ALLIED CHEMICAL GYPSUM	NATURAL GYPSUM
LOI	.71	.99
SiO_2	20.61	20.52
$A\ell_2O_3$	6.32	6.29
Fe_2O_3	2.03	2.07
CaO	63.53	63.14
MgO	2.78	2.78
SO_3	2.48	2.62
K_2O	1.19	1.21
Na_2O	.23	.24
Cl	.07	.06
Insoluble	.10	.23
C_3S	49.5	47.8
C_2S	21.8	22.8
C_3A	13.3	13.2
C_4AF	6.2	6.3

LOI - Loss on Ignition
C_3S - Tricalcium Silicate
C_2S - Dicalcium Silicate
C_3A - Tricalcium Aluminate
C_4AF - Tetracalcium Aluminoferrite

TABLE 1

PHYSICAL RESULTS

TEST #1

1982 12 15

TYPE 10 CEMENT

	Allied Chemical Gypsum	Natural Gypsum
Blaine m^2/kg	324	331
Residue % 75µm	1.6	3.0
Vicat Set min.	140	135
False Set %	96.4	88.2
Air Content %	9.0	9.5
Autoclave Expansion %	.13	.13
Compressive Strength MPa		
1 Day	13.1	12.7
3 Day	21.1	21.2
7 Day	25.7	23.7
28 Day	31.8	29.2

TABLE 2

CONCRETE RESULTS

TEST #1

1982 12 15

TYPE 10 CEMENT

		ALLIED CHEMICAL GYPSUM	NATURAL GYPSUM
Mix Design kg/m³			
Cement		255	255
Coarse Aggregate		1068	1068
Fine Aggregate		884	884
Water		162	163
Slump mm		85	85
Compressive Strength MPa			
1 Day		10.4	10.4
2 Day		24.0	22.2
7 Day		28.7	27.0
28 Day		35.3	32.6
Setting Time (Penetration Resistance) MPa			
4 hr		0.2	0.6
5 hr		1.8	2.6
6 hr		4.3	8.3
7 hr		7.7	15.2
7.5 hr		32.5	36.4
Initial Set	3.5 MPa	5.9 hr	5.4 hr
Final Set	27.6 MPa	7.6 hr	7.3 hr

TABLE 3

CHEMICAL RESULTS

TEST #2

1983 07 19

TYPE 10 CEMENT

% COMPOSITION	ALLIED CHEMICAL GYPSUM	NATURAL GYPSUM
LOI	.61	.69
SiO_2	20.36	20.54
$A\ell_2O_3$	6.12	6.41
Fe_2O_3	2.07	2.04
CaO	63.69	63.83
MgO	2.60	2.71
SO_3	2.92	2.98
K_2O	1.29	1.28
Na_2O	.24	.24
Cl	.08	.08
Insoluble	.13	.22
C_3S	52.1	49.2
C_2S	19.2	21.8
C_3A	12.7	13.5
C_4AF	6.3	6.2

LOI - Loss on Ignition
C_3S - Tricalcium Silicate
C_2S - Dicalcium Silicate
C_3A - Tricalcium Aluminate
C_4AF - Tetracalcium Aluminoferrite

TABLE 4

PHYSICAL RESULTS

TEST #2

1983 07 19

TYPE 10 CEMENT

	ALLIED CHEMICAL GYPSUM	NATURAL GYPSUM
Blaine m²/kg	363	361
Residue % 75µm	.5	1.4
Vicat Set min.	133	112
False Set %	100.0	85.7
Air Content %	11.0	9.6
Autoclave Expansion %	.16	.17
Compressive Strength - MPa		
1 Day	15.8	17.2
3 Day	24.4	26.1
7 Day	29.0	29.3
28 Day	34.6	35.0

TABLE 5

CONCRETE RESULTS

TEST #2

1983 07 19

TYPE 10 CEMENT

	ALLIED CHEMICAL GYPSUM	NATURAL GYPSUM
Mix Design kg/m³		
Cement	255	255
Coarse Aggregate	1068	1068
Fine Aggregate	884	884
Water	164	167
Slump mm	85	85
Air Content %	2.4	2.3
Compressive Strength MPa		
1 Day	17.6	17.1
3 Day	25.5	25.6
7 Day	29.6	29.2
28 Day	34.5	34.0
Setting Time (Penetration Resistance) MPa		
3 hr	.8	1.1
4 hr	5.5	7.7
5 hr	23.2	25.4
5.5 hr	41.9	42.7
Initial Set - 3.5 MPa	3.8 hr	3.6 hr
Final Set - 27.6 MPa	5.1 hr	5.1 hr

TABLE 6

GYPSUM ANALYSIS

	ALLIED CHEMICAL GYPSUM	NATURAL GYPSUM
% Free Water	3.4	3.8
% Combined Water	14.2	17.0
% SO_3 Total	42.0	41.0
% SO Gypsum	31.6	37.8
% SO_3 Anhydrite	10.4	3.2
% Gypsum	67.8	81.2
% Anhydrite	17.7	5.4
% Insoluble	2.7	5.8
% as $CaSO_4$	71.4	69.7

All analysis reported on Combined Water Basis.

TABLE 7

CONTRACT SERIAL NUMBER 1SQ79-00156
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DEVELOPMENT OF BY-PRODUCT FLUOROGYPSUM FOR SALE

ALLIED CHEMICAL CANADA, LTD.
DIVISIONAL TECHNICAL DEPARTMENT

OCTOBER, 1982

REPORT TDA-R82-8

135 pp + pictures

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Report TDA-R81-8

ALLIED CHEMICAL CANADA, LTD.

DIVISIONAL TECHNICAL DEPARTMENT

DEVELOPMENT OF BY-PRODUCT FLUOROGYPSUM FOR SALE

SUMMARY

For the past twelve years, by-product fluorogypsum has been impounded in a disused limestone quarry close to Allied Chemical Canada's Hydrofluoric Acid production facility at Amherstburg, Ontario. A study of alternative disposal possibilities was started in 1978 because the quarry will be completely filled by 1984.

This report reviews studies carried out on the preparation of this fluorogypsum for use as portland cement additive at pilot operations in Amherstburg and supporting research work carried out by the Ontario Research Foundation in Mississauga, Ontario.

The work by ORF established the basic physical and chemical parameters of gypsum suitable for the cement industry and field tests have confirmed them for Allied Chemical fluorogypsum.

Theoretically, 67% of the 220,000 tons per year of the fluorogypsum is suitable for cement manufacture. Yield in extended field tests to date has been in the order of 30%, experienced during runs considerably below the capacity of the plant.

More importantly, the 33% by mass of unsuitable material occupies 75% of the total volume of the by-product and hence sale of gypsum reduces but does not solve the impounding problem.

Associated studies provided the basis for a proposal to close-out or "cap" an old soda ash waste bed with gypsum and at the same time provide 20 years of storage capacity for gypsum. Thus, two problems appear to have been resolved.

We will install a large scale test system during the winter of 1982-1983 to determine the economic optimum combination of closure - storage - sale parameters.

I. INTRODUCTION

A. Manufacture of Hydrofluoric Acid

Allied Chemical Canada, Ltd. manufactures hydrofluoric acid at Amherstburg, Ontario, by the reaction of finely ground fluorspar (CaF_2, typically 90 + % - 100 mesh) with concentrated sulphuric acid (H_2SO_4). This reaction may be represented as follows:

$$CaF_2 + H_2SO_4 \longrightarrow 2\ HF\uparrow + CaSO_4$$

The hydrofluoric acid, produced as a gas, is condensed and purified to yield anhydrous HF. The by-product calcium sulphate ($CaSO_4$) is formed as a powder which agglomerates to pellets and balls before discharge from the reactor. This "residue" contains small amounts of unreacted fluorspar and sulphuric acid as well as traces of HF. The acidic solids are slurried with about 350 m^3/hr of water for transportation and neutralized with a process waste stream (brine muds) consisting primarily of calcium carbonate ($CaCO_3$) suspended in a sodium chloride brine solution. This mixture is pumped to an OME approved solids impoundment area (a portion of a previously worked-out Allied limestone quarry - see photos, Appendix 1).

A typical chemical analysis of the residue is compared with those for three natural gypsums in Table I.

B. Fluorogypsum Impoundment Area

The solids are allowed to settle and fill the impoundment area while the decanted water is recycled to the plant for use in moving more residue.

The impound area available is 6 hectares in size. At capacity, the HF plant will produce fluorogypsum at an equivalent rate of 1.23×10^5 m^3 per year, or over 2 meters of depth per year over the entire pond. In 1978 it was projected that the site would be full by 1984. However, increases in production have shortened the expected time schedule to late 1983.

Several alternates have been considered to provide a method of gypsum disposal, these include:

1. Removal of gypsum previously ponded to another site.

   This would provide additional space in the present impound area and is estimated to cost roughly $500,000 per year.

2. Providing additional dykes around and within the borders of the present site, at a cost of $1.5 million. The new dyke would fill in three years and would make additional dyking impossible, thus a new pond site would have to be found at that time.

3. Preparation of newly deposited gypsum for sale as a by-product.

4. More recently, a plan has evolved for deposition of the gypsum directly on top of our adjacent soda ash waste facility storage pond which is presently being closed-out.

C. Possible Use in Cement Manufacture

To develop a potential route of disposal which would cover cost of such disposal and also provide alternate supply of gypsum for portland cement companies, initial contacts were made with St. Lawrence Cement Co. Their requirements for chemical purity and physical characteristics were discussed.

Due to the nature of Allied's manufacturing process, the waste material is deposited in distinct layers.

Particles in two size ranges are produced, as noted in Figures 1a and 1b.

Initial samples taken from the available gypsum revealed the following:

1. The material was of sufficient chemical purity. (See St. Lawrence specification sheet, Table II).

2. The anhydrite was sufficiently hydrated to meet the St. Lawrence requirement.

3. Due to the size range characteristics, the material was deposited in layers which were very loosely held together.

   The lack of cohesiveness was seen as a deterrent to direct harvesting of this previously ponded material.

Bench scale tests showed that fresh anhydrite, with sufficient water present and given a reasonable timeframe, readily hydrates to form hard rock-like material (gypsum).

A pilot scale test was arranged to separately impound a section of residue for hydration, and to subsequently remove and size the resulting gypsum for shipment to St. Lawrence.

II. PILOT SCALE TESTING

Trials 1 to 3 involved a small scale pond roughly 30m by 50m by 1m deep. This was built on top of the main gypsum pond as shown in Figure 2. The chemical analyses of residue composites for each trial are shown in Tables III, IV and V.

A. Trial 1

The first trial collection was made in August, 1978. The material was ripped and screened in September. Yield was 700 t at 76% $CaSO_4 . 2 H_2O$. The sample was shipped to St. Lawrence for testing. Their results were promising and warranted a second test trial.

It was noted in the first trial that proper neutralization of the residue was critical to ensure control within pH specifications. Thus, the addition of a neutralizing medium was critical to ensure an acceptable product. It also was noted that the flow of slurry into the main pond while the test batch hardened, interferred with test pond dewatering. This was thought to cause the low $CaSO_4$ yield.

B. Trial 2

The second collection was made in November 1978. The sample was allowed to harden into winter, and several attempts were made to determine when the material was hard. At this point it was assumed a "hardened" pond was equivalent to a "hydrated pond". Sonic measurements showed velocities in the range of hard gypsum but readings could also indicate ice, i.e. frozen material rather than hydrated (and thus hardened). Subsequent ripping in January, 1979 revealed some very hard material which led to the first use of a D9 dozer with a one-tooth ripping attachment (note Photographs, Appendix 2). Regions of sloppy material where no material cohesion had taken place, were encountered upon harvesting. These regions appeared to be unhydrated (unhardened) partially dewatered anhydrate sludge. This trial collected 2600 t of low quality gypsum (50% $CaSO_4 . 2 H_2O$). Upon crushing and screening, yield was 800 t of product suitable for shipment to St. Lawrence.

The noted problems were:

(1) non-uniform winter hardening (in the form of sections of the pond which froze but did not consolidate) and (2) the difficulty of harvesting the very hard material.

C. Trial 3

The third collection was in March 1979, with ripping in May of that year. This was a successful trial and yielded 73% $CaSO_4 . 2 H_2O$. It led to the first indications that the segregated sections of fines and coarse were characterized by markedly different rates of hydration and hardening.

III. FULL SCALE TESTING - DEVELOPMENT OF A PLAN

The first full scale test took place in November, 1979. An 18000 t pond approximately 65m square by 2.5m high was constructed with gypsum dykes on three sides and a clay dyke surrounding the entire pond to contain recycle water as shown in Figure 3. The material was kept covered with water to allow hydration by means of a controlled weir. The pond was filled for a month before system problems forced discontinuance. About 15000 t of gypsum were collected during this run.

Two distinct areas were observed in the filled pond. One, close to the inlet point, essentially consisted of "golf ball" size particles with minor quantities of sand sized particles. The other, at the discharge end of the pond, largely consisted of the fine material in water suspension. The fine particles settled and accumulated in this area with very little loss of material.

Seismographic and surface tests were performed to record the hardening cycle. Ten weeks later, in January, 1980, the fines portion of the pond appeared to be hard enough for harvesting. Upon initial ripping with the D9 dozer, it was obvious that the material had been frozen on the surface. Once through the surface layer, the dozer uncovered a soft, mushy residue. The seismic velocity indications were thus not indicative of the bulk of the material.

At that time only one-half of the material was harvested. That portion of the pond was renewed for another small batch test. When, after six months had passed, the remainder of the pond was harvested, it was found that the bulk of the large particle bed was indeed rock-hard, that it had hydrated and hardened into one contiguous mass. Pieces removed ranged up to 1 to 2m in size, about five tonnes.

The results of this test pointed to the fines as a problem. The question was how to mix the fines with the coarse uniformly to duplicate a microscale test where the mass hardens solidly. No economical method was found to overcome this problem.

The next full scale trial was conducted in the one-half pond emptied previously. Drainage tiles were placed at the bottom of the pond and covered by a gypsum layer. This hopefully would allow water to leave the pond and thus facilitate dewatering and eventual hardening of the pond.

Upon filling the pond it was noted that the fines were being removed with the water through the drainage system. Filling was allowed to continue until the fines plugged the drains and began to accumulate in the pond. The hardening was more extensive in this run because a greater proportion of coarse material was retained. Again, very large lumps were removed upon harvesting, but the fines did not harden.

Seismic studies were not attempted in this test. Instead, a core driller was used to extract sections of each bed. This proved to be a more positive method for determining the degree of hardening.

IV. R & D - ONTARIO RESEARCH FOUNDATION

At this point it was decided to engage the Ontario Research Foundation to further study the hardening and hydration rate phenomena. Initial contacts with ORF were directed toward defining the characteristics of the mechanisms involved in these two phenomena.

Dr. Robert Bruce and Ms. Lydia Luckevich of ORF undertook to define the parameters necessary to provide control over the hydration and hardening processes. Their initial attack was to define a chemical agent that would disperse the fines among the coarse material to thus facilitate overall hardening. ORF used screens to simulate the segregation of the coarse/fine fractions. It was found that the coarse layer alone, neutralized with brine muds, hardened and hydrated within two weeks.

A summary of the ORF study is included as attachment B. A hydrocyclone was selected as a relatively inexpensive unit for separating the coarse and fine particles at the gypsum pond. The model selected was manufactured by Krebs Engineers, No. D20LB, with a rated capacity of 400 m^3/hr at a pressure drop of 83 kPa. ORF studied the rough yield of coarse fraction we could expect from the hydrocyclone, and found that the coarse fraction comprised 67% of the mass of residue (greater than 60 μm particles), but that the fine fraction occupied 75% of the volume that the full residue occupied. Thus, a significant portion of the output would be available for sale as by-product gypsum, but our problem of waste bed space would not be significantly helped by this scheme. Nevertheless, it was the only reasonably economic approach at hand.

Plans went forward late in 1980 for full scale testing of the hydrocyclone concept.

V. REVISED PLAN - FULL SCALE TESTS

The 60 µm size split desired was well suited to a single cyclone that would handle the full process flow. With delivery and installation of the cyclone taking several months, it was late April, 1981, before the next test was started.

The coarse cyclone underflow was a very thick mud (40% to 80% solids). The run was terminated after 4 h. It later was determined that the total flow had been restricted by the feed line pressure drop, thus causing the residue to back up at the plant.

A second, dual feed line test was run for about 24 h before system drainage problems forced a shutdown. A large quantity of solids accumulated at the cyclone underflow. The material did not flow into the pond as anticipated, but instead accumulated at the discharge of the cyclone. A water flush was devised to carry the coarse particles into the pond.

A third run was successful in obtaining about 2200 t of coarse residue. However, harvesting was delayed from spring into the summer of 1982.

Cores from the coarse side of the pond were tested extensively by ORF and results are noted in their attached report. They show strength development is fairly rapid in the first 3 to 4 weeks after deposition. About 75% of the ultimate strength is developed during this period. This would be the optimum point at which harvesting should be accomplished (to avoid ripping the gypsum when at full strength). After harvest, local storage would allow strength development to a maximum.

Ripping and screening operations were carried out throughout the spring and summer of 1982. The material showed no degradation on exposure to weather after hydration and hardening. A screened batch of about 1000 t is ready at this writing for shipment to St. Lawrence for their process and storage tests. This batch is the best available to date with regard to uniformity of sizing.

VI. DISCUSSION - MAJOR PROBLEMS

The major problems encountered and decisions faced throughout this project fall into these categories:

A. Fine Fraction vs. Coarse -- Separate or Mix.

B. Hardening and Methods of Determining of Hardness.

C. Methods of Harvesting and Product Sizing.

D. Winter Hardening.

A. Fine Fraction vs Coarse — Separate or Mix

It became clear after the initial full scale test that the fine fraction would not harden properly on its own. The $CaSO_4$ content was lower than the coarse fraction, but not significantly so, however it varied widely from sample to sample. The cause of these inconsistencies was not clear, but it did not seem to be a contamination problem. Later ORF studies showed that $CaCO_3$ (brine mud) contamination slows the granular growth, essentially causing formation of discrete particles of gypsum and slowing the hardening process.

A mixed sample extracted from the residue feed stream would harden completely under indoor conditions in 2 to 3 weeks. Thus, it was possible to include the fines with the coarse to obtain an acceptable product if the fines were distributed evenly throughout the pond rather than being concentrated as in the fine fraction. However, this would be difficult to accomplish on a large scale. Various schemes were considered, including:

1. Mechanical mixing with a small dozer at regular intervals during pond filling.

2. Location of a drag bucket over the pond to mechanically mix the contents several times during filling.

3. Distribution of pond feed to several points to minimize the flow pattern and thus allow the coarse and fines to collect in alternating and overlapping layers.

Each of these was seriously considered but rejected due to its unworkable nature in a full scale production run.

Our first suggestion to ORF was possible use of a flocculant to agglomerate the fines. However, initial investigation showed that the particles exhibited flocculating properties of their own and that the additional flocculant did not help agglomeration.

To overcome the strong agglomeration tendency, and afford the particles some individual behavior, work was then directed towards use of a dispersant. This would allow the individual particles of anhydrite and muds to intersperse freely. The final concentrations and material selection proved expensive and the logistics of continuously injecting dispersant was not practical in a long-term production effort.

The concept of hydrocloning arose during discussions of the treatment of the fine and coarse fractions. The idea of collecting the coarse fraction alone arose when it was found that the coarse fraction would harden within 2 weeks, while the fines took much longer and developed much less strength. Work was then directed at determining the yield of gypsum and the various hardening/hydration characteristics of screened portions of neutralized residue.

Further work, including core sampling, was done in the field to collect data at various times from actual runs. Core samples taken at intervals during hardening showed the major strength development took 3 to 4 weeks with maximum strength being reached at seven weeks. This period for strength development would be satisfactory in the overall filling/hardening/harvesting cycle.

The most recent test collection and subsequent harvesting trials have shown the separation of the residue into coarse/fine fractions to be the simplest most economic of ponding methods from a continuous production standpoint. No additional manpower is necessary to operate the system. Once in run, the fractions separate by themselves and the collection of coarse material is accomplished while the fine fraction is piped around the collection pond to the drainage trench, with the recycle water being returned to the main pond. Some checking on a per shift or per day basis is necessary to ensure that the coarse hydrocyclone underflow is being carried away from the cyclone discharge. Thus, with properly designed cyclone and pond to handle the anticipated flows and with adequate ponds to alternate collection points, the continuous collection of gypsum for sale could be readily achieved.

B. Hardening and Methods of Determining Hardness

Initially, seismographic studies were used to determine the hardness of gypsum and its suitability for harvesting. It was thought that seismic results could be used to determine when the material approached a nearly complete state of conversion to gypsum.

The first trial was a summer run, and hardening was completed rather rapidly during a seven week period. The second trial was a winter run, and hardening was inhibited by freezing and also by cross flow of fresh residue, thus determination of hardening at the discharge end of the pond was difficult. Some of the material which appeared hard before harvesting, changed into mush when warmed. This was the first indication that winter hardening was a problem. Longer aging was seen as the answer at that time.

The first commercial scale pond test again used seismographic techniques to determine hardness. This was in mid winter and the material was collected over a greater depth than previous tests. Also, the separation of coarse and fines was much more pronounced in this trial.

Indications were that the fines section was "hard". Both seismic and physical surface breakage suggested that the material in the pond was a contiguous mass.

Upon harvesting the top layer (0.3 m thick) and breaking through to the material beneath, it was obvious we had been mistaken. The material became mushy when being worked with the D9 dozer where we had expected to find hydrated/hardened gypsum. The dozer easily removed the material, there being no great resistance to its passage. After this trial the seismic method was abandoned.

A more positive method, core drilling, was used in all other trials. This proved to be less costly, quicker and a much better indicator of sub-surface condition and was recommended for all further work.

The speed of penetration of the core drill can be used as an indicator of relative hardness of successive layers encountered. The cores can also be retained for interpretation of the layered structure and the composition of layers vs hardness and degree of hydration.

C. Methods of Harvesting and Product Sizing

In the first trials, a large loader was used to separate and remove successive layers. The material was piled using a payloader. All the gypsum was removed and good product separated for shipment. A dozer was used to crush the large, 2m chunks before shipment. It was recognized that a better method was needed to produce a more uniform product.

Consultation with surface mining experts led to the use of a D8 or D9 dozer with a modern ripper attachment. This machine plus a front end loader probably could remove and stockpile the entire pond (7000 t) in 3 to 4 days.

The third pilot trial and the first three large pond trials were ripped using a D9 dozer. Experience with this method was not as good as expected. Several passes were necessary, each ripping about 15 to 20 cm in depth 1 to 2 m wide. Due to the weight of the dozer, the product contained an excessive amount of fines. It was known that fines in the product were not acceptable because they would tend to form a slippery sludge upon exposure to wet weather and subsequently would cause problems during crushing at the cement plant.

This method of harvesting was continued until November 1981. At that time, a local contractor suggested use of a Wain-Roy bucket with ripper teeth attached for harvesting. This was purchased and proved to be the best method for avoiding fines during harvesting. It was used to remove the last coarse collection and resulted in better than 60% yield plus 5 cm size on ripping. However, about half of the ripped material was greater than maximum desired size of 20 cm and had to be crushed. This generated more fines and the overall yield of on specification material was only about 50%. It is planned to use the rejected fine material to line the bottom of the collection pond. Upon contact with the newly deposited coarse material, the fines will form a hard mass which can, in turn, be harvested to yield 50% as product. Thus, each harvest will yield an amount of new material equal to that deposited and the remaining fines will be continuously recycled.

Screening of the harvested material to the 5 to 20 cm size acceptable to St. Lawrence was attempted only on the last test batch of coarse material collected. The screening operation and associated crushing operation have not been optimized as to cost due to the problems encountered with each run and the less than optimum yield on each previous run. Further work in these areas will be necessary before the project can proceed to commercial production.

In early summer 1982, contacts were made with CIL Explosives Division personnel. They were consulted as to the use of explosives to "pop" the gypsum and, hopefully, to obtain a uniformly sized material suitable for removal to a screening operation. They expressed the desire, upon viewing our facility, to conduct a test blast on the main gypsum pond for the purpose of obtaining data on the blasting characteristics of this material.

These data would be used to predict the behaviour of the material on blasting and to establish a possible blasting pattern and charge size for use by Allied to harvest the material. A test was arranged on this basis for September 9, 1982. As noted in the CIL report (note Attachment 4), the test was sufficiently successful to conclude that this would be an efficient method to prepare the material for harvesting. The test covered a range of blast conditions, ranging from cracked surface to a 4 x 2 m crater which contained considerable powered material. A crater slightly smaller in size yielded an estimated 60 to 70% in the 5 to 20 cm range.

This method is seen as the most efficient and easily controlled of the methods available. It is recommended along with screening and return of fines to the collection pond as the optimum method for gypsum harvesting.

D. Winter Hardening

Of the major problems discussed, the hardening of the gypsum in winter is the only factor that can not be dealt with in a continuous production scale facility. It was shown by ORF that the hydration process slows during the cold weather.

Hydration does proceed fairly rapidly above the freezing point. Thus, if the ponded material does not freeze for roughly two weeks, the chance of pond hardening is greatly increased. There are, however, three months in winter still in question. Further study in full scale collection is warranted to develop methods for dealing with this period. Increased holding capacity to retain this material would be required. When warm weather returns, hydration would again take place, until the material reached a state where it could be harvested.

VII. ECONOMIC ASSESSMENT

The costs for harvesting and screening the gypsum for a typical pond area 65 m square, by 2.0 m deep, are broken down as follows:

1.	Drilling 2 m holes x 100 mm on a grid pattern 3m x 3m		$ 3,000
2.	Loading explosives in successive rows		1,000
3.	Cost of explosives @ $2/kg, 4.6 kg/hole		4,000
4.	Set up screen		6,500
	Total one time items		$14,500
5.	Cost of operating screen, with one loader @ 1000 t/d		$ 500/d
	Above applied to screening yield of 6,000 t on total harvest of 12000 t		
	Set up - $14,500/6,000 t	=	$ 2.41/t
	Operating - $500/d per 1000 t/d @ 50% recovery	=	1.00/t
	Total cost to harvest		2.41/t
	Transportation of 6000 t to local storage @		2.50/t
	Total Allied Cost		$ 5.91/t

The total cost of recovery of gypsum is thus $5.91/t.

Current disposal costs are minimal, including operation and maintenance of pump and pipeline approximately 1 km to the waste pond. However, with the waste pond almost full, the cost of dyking and/or hauling material to another site becomes prohibitive and the sale of fluorogypsum becomes more attractive.

VIII. CONCLUSIONS AND RECOMMENDATIONS

The conditions under which gypsum of sufficient purity to meet St. Lawrence Cement specifications have been defined by Ontario Research Foundation and demonstrated in full-scale field testing.

This includes separation of a coarse fraction which will show:

a. Sufficient hydration to meet 78% minimum gypsum content

b. Sufficient strength development to allow harvest of the material within a seven week cycle period, during 9 months of the year.

c. Minimized contamination from the high carbonate fraction of the fine material.

These conditions are sufficient to yield a gypsum ready for harvest and subsequent shipment during nine months. The approach for the remaining 3 winter months has yet to be defined. These questions will be answered by testing during the winter of 1982/83 on the soda ash waste bed.

Harvesting and preparation for shipment have been accomplished during recent tests, using the various methods under study. The most economical and efficient to date is by use of sequential explosive charge detonation to free the gypsum in successive rows. The material, as blasted, is ready for screening and loading. The screening can be accomplished at a rate of up to 1000 t per day.

The parameters are now well defined for production of by-product fluorogypsum for use in cement manufacture. Note the testing program outlined by St. Lawrence Cement, Attachment C. Their schedule calls for Type 10 cement to be produced using fluorogypsum and natural gypsum rock simultaneously. The two resulting cements will be tested separately for chemical and physical characteristics as specified under the A5 Portland Cement standard. Also, laboratory preparations of concrete will be made from the same cements.

The second phase of testing involves outdoor storage of the fluorogypsum through the winter and retesting in the spring.

From Allied Chemical's point of view, there is a potentially more cost effective alternative use for the material. Use of this gypsum as capping material on the closed-out soda ash waste bed is now planned, possibly in conjunction with sale of gypsum for cement manufacture.

The "capping" test during the winter of 82/83 will determine the relative costs of possible alternatives. A final plan for disposal, based on this study, will then be formulated.

R.L. Shaw

R.L. Shaw - P. Eng.
For Allied Chemical Canada, Ltd.

TABLE 1

CHEMICAL ANALYSES

Natural/Synthetic Gypsum - Typical Analyses

	SAMPLES FROM ST. LAWRENCE CEMENT			
	Nova Scotia Gypsum	Nova Scotia Anhydrite	Caladonian Gypsum	ACCL FLUOROGYPSUM
	wt %	wt %	wt %	wt %
$CaSO_4$	71	92	67	95 to 98.5
$CaCO_3$	16	5	18	0.6 max.
$MgCO_3$	8	0.5	8	0.4 max.
SiO_2	3.8	1.7	5.0	0.8 max.
Other metals as oxides	1.0	0.8	1.2	0.6 max.
CaF_2	0.1	0.1	0.1	0.2 to 2.0
Chloride	0.1	0.1	0.1	1.0 max.

Note: Analyses for dried samples (250°C)

TABLE II

SPECIFICATIONS FOR SYNTHETIC GYPSUM

ST. LAWRENCE CEMENT CO.

NaCl (calculated from total chlorine)	1.0% max.
pH	6.8 - 7.8
Heavy metals	2.0% max.
$CaSO_4$	78% min.
CaF_2	3% max.
Preferred size*	100 to 300 mm

* Size requirement subsequently changed to 50 - 200 mm, nominal due to method of screening and tendency toward oversize.

TABLE III

TRIAL COLLECTION NO. 1

August - September, 1978

ANALYSIS OF RESIDUE COMPOSITE

		St. Lawrence Cement Specifications
% H_2O	21	
Analysis Dry Basis		
F^- as % CaF_2	2	3 max.
Cl^- as % NaCl	1	1.0 max.
Heavy metals	1	2.0 max.
% $CaSO_4$	96	78 min.
pH of 10% solution	8.4	6.8 - 7.8

TABLE IV

TRIAL COLLECTION NO. 2

November, 1978 - January, 1979

ANALYSIS OF RESIDUE COMPOSITE

% H_2O	21	
Analysis Dry Basis		St. Lawrence Cement Specifications
F^- as % CaF_2	2.2	3 max.
Cl^- as % NaCl	0.1	1.0 max.
Heavy metals	0.1	2.0 max.
% $CaSO_4$	71	78 min.
pH of 10% Solution	8.5	6.8 - 7.8

Dried at 45oC for 2 hours - apparent free moisture 5.64%.

TABLE V

TRIAL COLLECTION NO. 3

March - May, 1979

ANALYSIS OF RESIDUE COMPOSITE

% H_2O - 21.2

Analysis Dry Basis		St. Lawrence Cement Specifications
F^- as % CaF_2	3.2	3 max.
Heavy Metals	1.0	2.0 max.
% $CaSO_4$	94.0	78 min.
pH of 10% solution	8.5	6.8 - 7.8

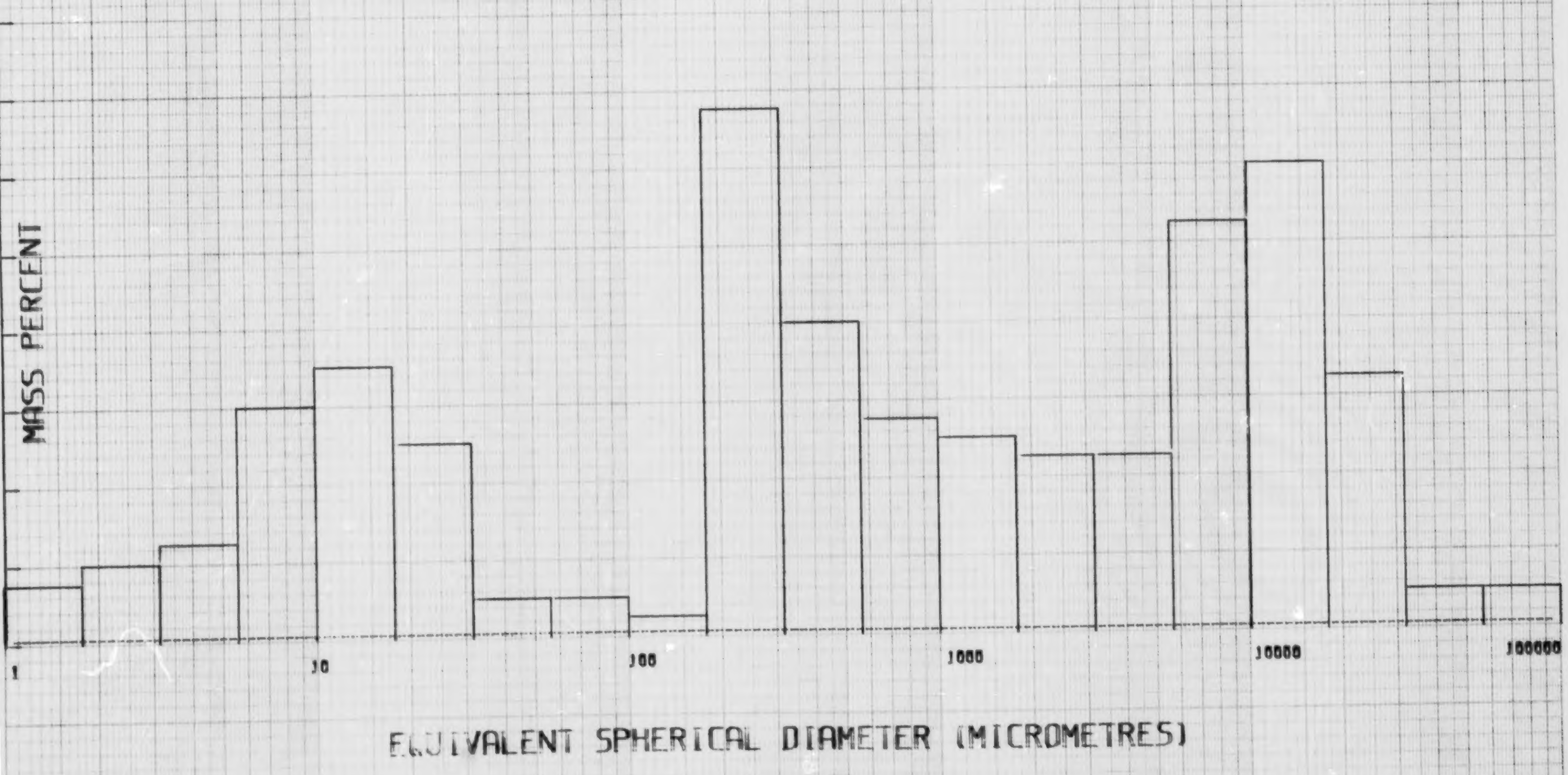
Chlorides analyzed on an individual basis:

Sample	Cl^- as NaCl, %	Sample	Cl^- as NaCl, %
1	0.1	9	0.1
2	0.1	10	0.1
3	0.1	11	0.1
4	0.2	12	0.1
5	0.1	13	1.8
6	0.1	14	0.2
7	0.1	15	0.2
8	0.1	16	0.7

K•E SEMI-LOGARITHMIC 5 CYCLES X 70 DIVISIONS
KEUFFEL & ESSER CO. MADE IN U.S.A.
46 6210

FIGURE 1A.

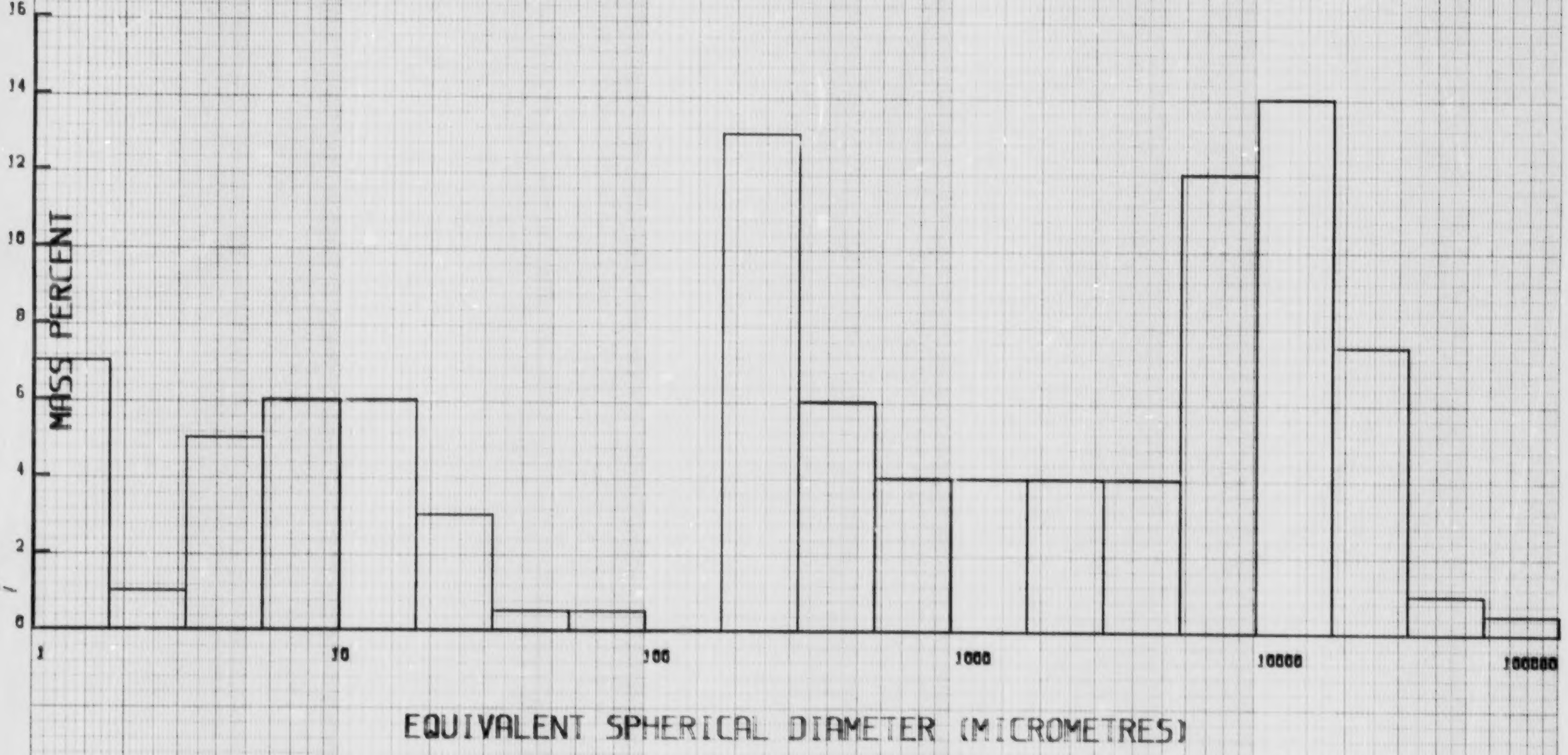
ARTICLE SIZE DISTRIBUTION FOR THE ANHYDRITE



K+E SEMI-LOGARITHMIC 5 CYCLES X 70 DIVISIONS
KEUFFEL & ESSER CO. MADE IN U.S.A.
46 6210

FIGURE 1B.

PARTICLE SIZE DISTRIBUTION FOR THE NEUTRALIZED SLURRY



K+E SEMI-LOGARITHMIC 5 CYCLES X 70 DIVISIONS
KEUFFEL & ESSER CO. MADE IN U.S.A.
46 6210

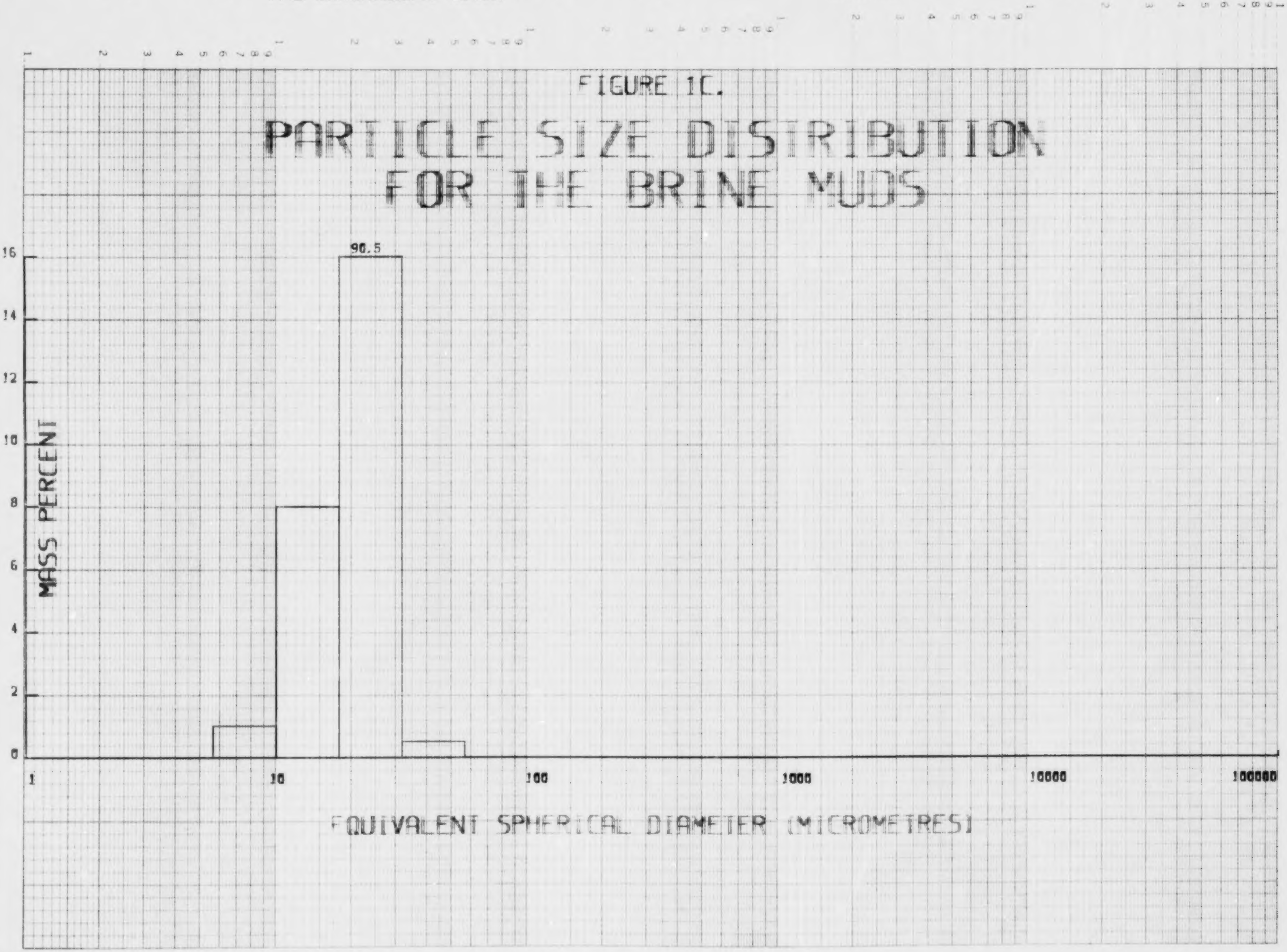
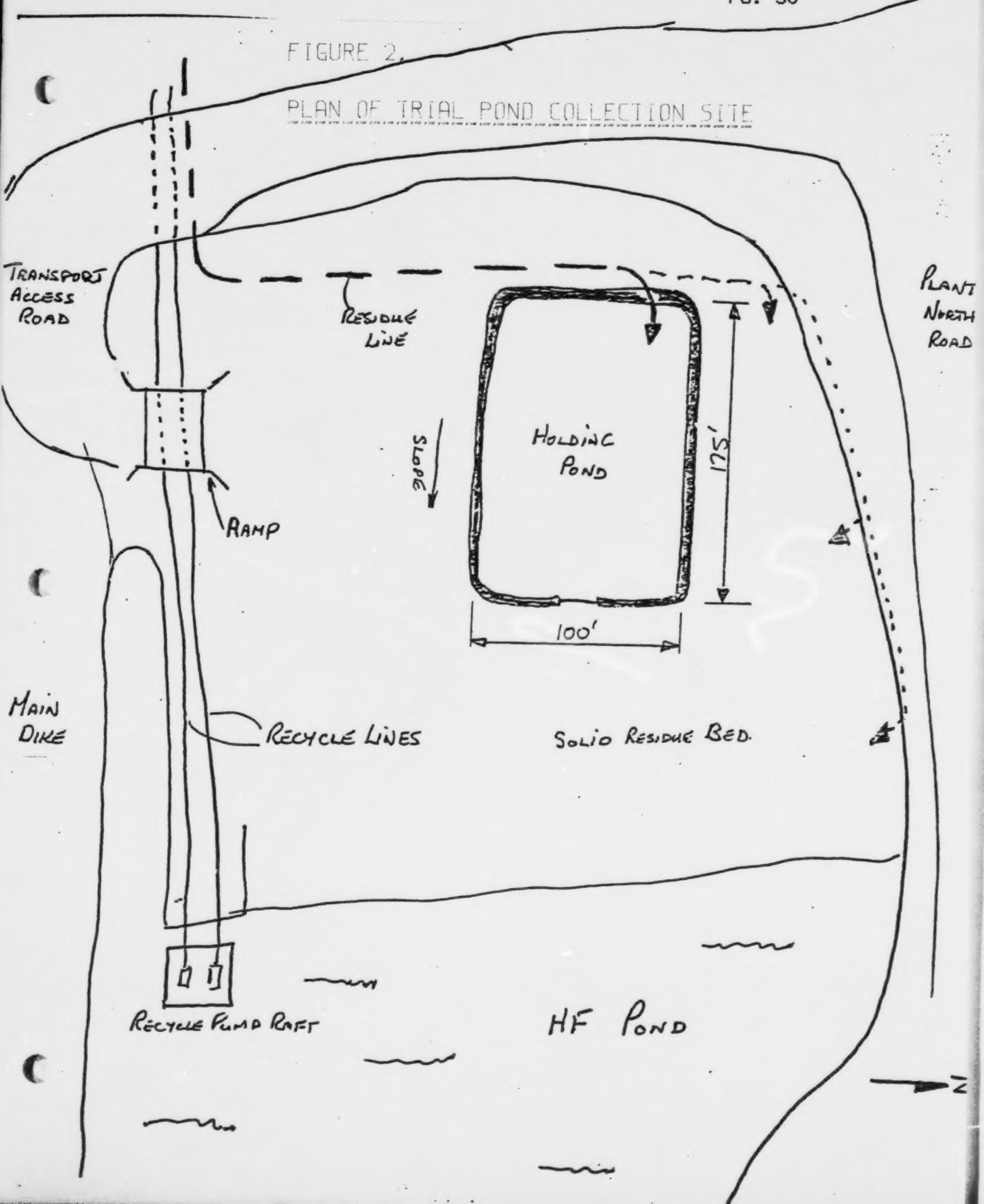


FIGURE 1C.

PARTICLE SIZE DISTRIBUTION
FOR THE BRINE MUDS

FIGURE 2.

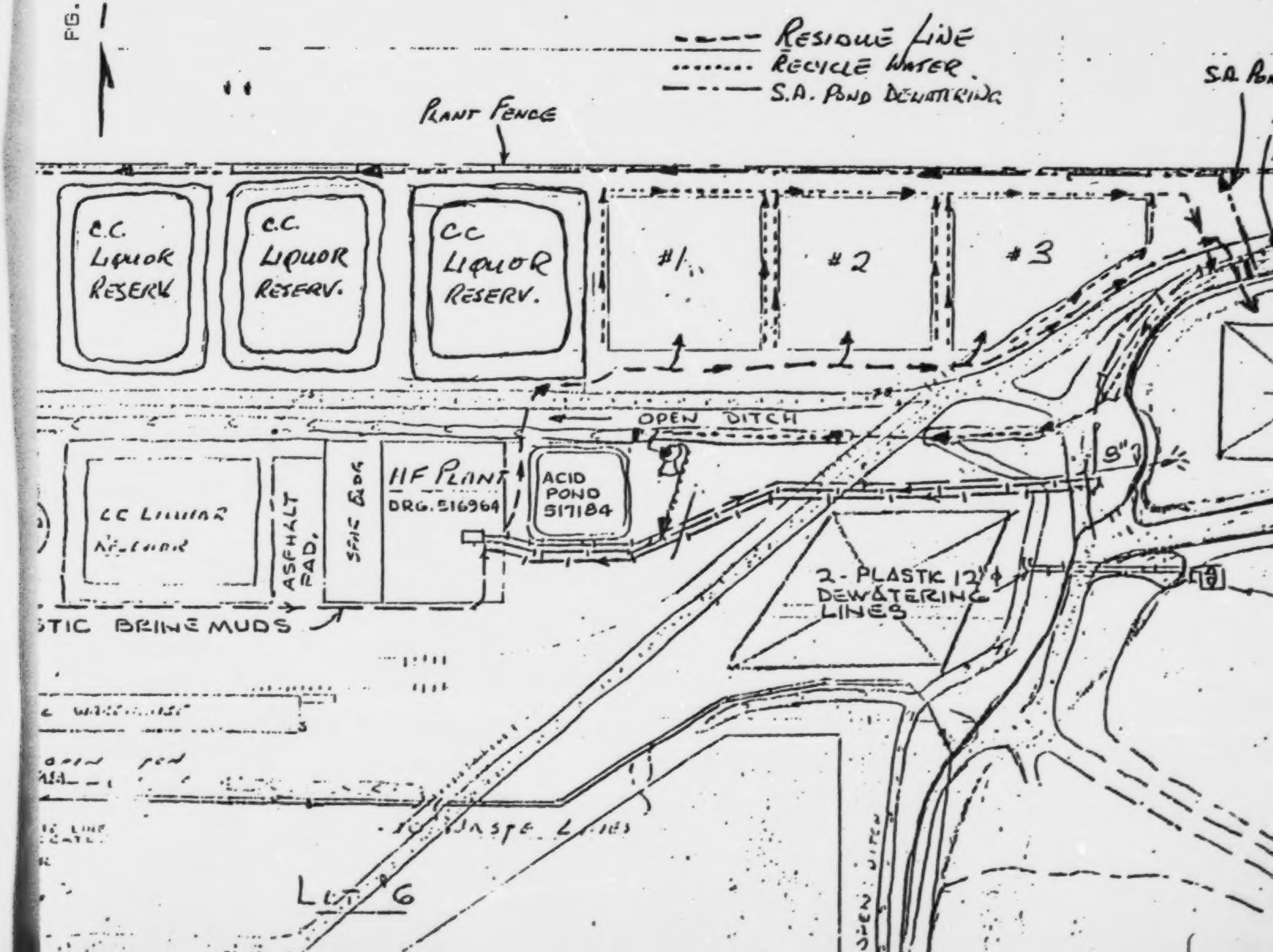
PLAN OF TRIAL POND COLLECTION SITE


TRANSPORT ACCESS ROAD
RESIDUE LINE
PLANT NORTH ROAD
HOLDING POND
175'
100'
SLOPE
RAMP
MAIN DIKE
RECYCLE LINES
SOLID RESIDUE BED
RECYCLE PUMP RAFT
HF POND
N

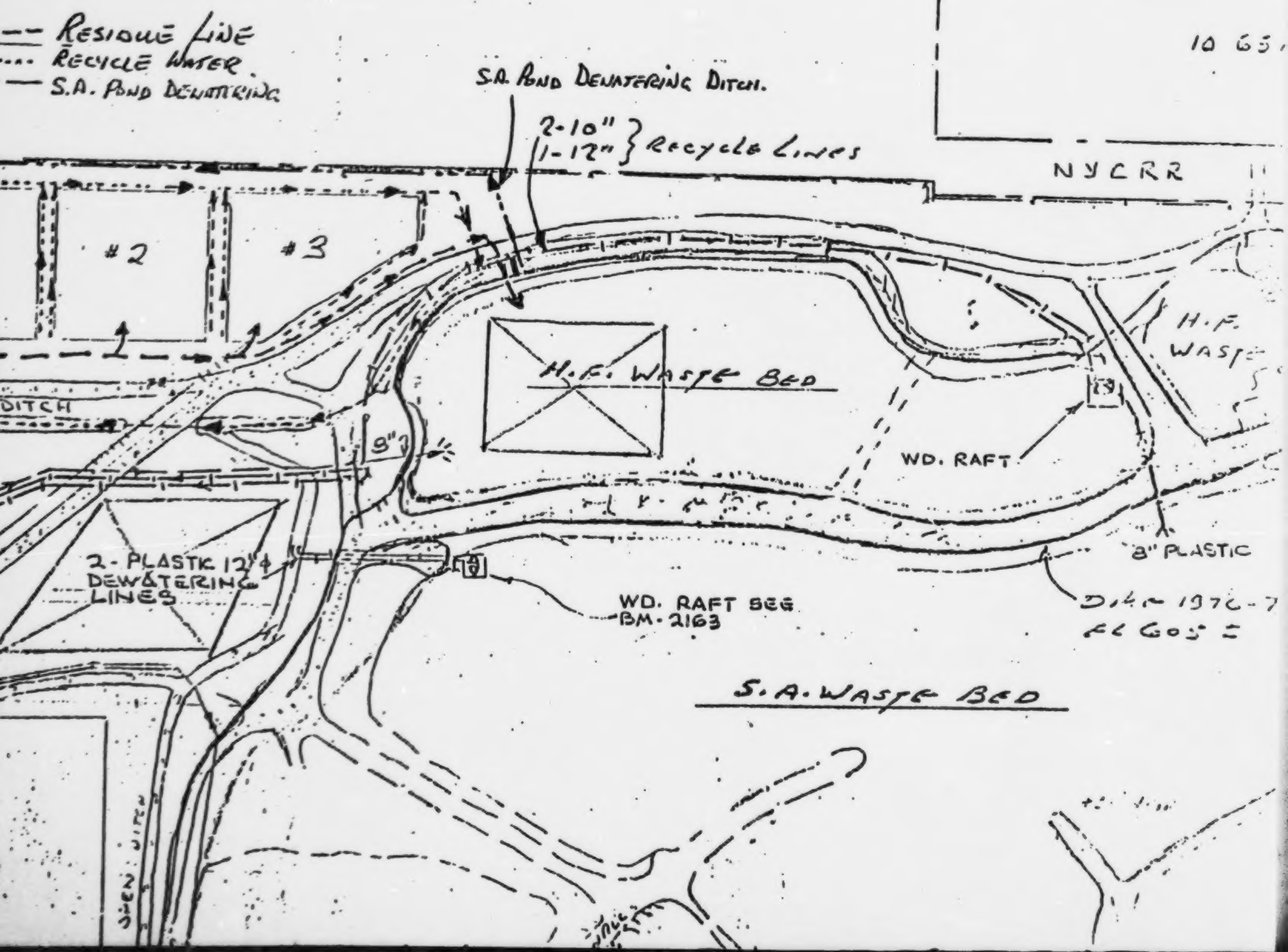
PG. 31

FIGURE 3.

PLAN OF FULL SCALE POND COLLECTION SITES


Residue Line
Recycle Water
S.A. Pond Dewatering
Plant Fence
S.A. Po
C.C. Liquor Reserv.
C.C. Liquor Reserv.
CC Liquor Reserv.
#1
#2
#3
Open Ditch
8"
HF Plant
DRG. 516964
Acid Pond
517184
CC Liquor Reservoir
Asphalt Pad
2 - Plastic 12" ø Dewatering Lines
stic Brine Muds
Waste Lines
Lot 6
Open Ditch

ULL SCALE POND COLLECTION SITES


-- Residue Line
.... Recycle Water
— S.A. Pond Dewatering
S.A. Pond Dewatering Ditch.
2-10"
1-12"
Recycle Lines
10 65
NYCRR
#2
#3
DITCH
H.F. Waste Bed
H.F. Waste
8"
WD. RAFT
8" PLASTIC
2-PLASTIC 12"φ DEWATERING LINES
WD. RAFT BEG BM-2163
Dike 1976-7
EL 605
S.A. Waste Bed

ATTACHMENT A

GOLDER ASSOCIATES - SEISMIC VELOCITY SURVEY

Golder Associates
CONSULTING GEOTECHNICAL AND MINING ENGINEERS

REPORT

TO

ALLIED CHEMICAL CANADA LTD.
SEISMIC SURVEY OF SYNTHETIC GYPSUM WASTE POND
AMHERSTBURG ONTARIO

Distribution:

2 Copies - Allied Chemical Canada Ltd.
Amherstburg, Ontario

2 Copies - Golder Associates
Mississauga, Ontario

March, 1980

791-1372

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2.0 PROCEDURE 1

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4.0 RESULTS AND DISCUSSION 2

5.0 CONCLUSIONS AND RECOMMENDATIONS 4

TABLE 1

SEISMIC VELOCITIES OF THE SYNTHETIC GYPSUM

FIGURES

1 - Site Location
2 - Typical Time-Distance Curves
3 - Time-Distance Curves for Surveys

1.0 INTRODUCTION

Golder Associates were retained by Allied Chemical Canada Ltd. to study the feasibility of using the seismic velocity of synthetic gypsum to determine when the solidifying material is in a form suitable for "ripping" and removal from the gypsum waste pond. The seismic velocity of the gypsum should increase as it hardens and therefore it may be possible to establish a correlation between seismic velocity and "rippability", and to thereby estimate a "characteristic" seismic velocity at which the synthetic gypsum is ready for removal.

Accordingly, consecutive surveys were carried out to assess the change in velocity of the synthetic gypsum during the early stages of hardening. In this report we describe the results and conclusions from these surveys.

1.1 Location

The site is located approximately one mile east of the Detroit River and northeast of the Town of Amherstburg. The adjacent Allied Chemical Canada Ltd. plant and facilities occupy a corridor of land stretching westward, towards the river (see Figure 1).

2.0 PROCEDURE

Surveys were conducted on December 20, 1979 and January 10, 1980. During each of these surveys, ten seismic spreads were placed in five locations as shown on Figure 3.

A geophone was placed at each location and hammer hits made at 5 ft. intervals away from the geophone, for up to 30 ft. At each location surveys were conducted in two directions at right angles, to assess any directional inhomogeneity in the seismic velocities. A Bison single channel, signal enhancement seismograph was used to measure the time of first arrival of the compressional seismic wave from each hammer point. The data is then plotted on time versus distance curves, and from these it is possible to estimate seismic velocities (see Figure 2a) of the surface material.

3.0 SURFACE CONDITIONS

The gypsum containing solution was placed in the pond from approximately October 4, 1979 to November 4, 1979. During the December 20 survey the material in the pond was slushy and slightly irregular. Three weeks later on January 10, the gypsum pond appeared to have consolidated to a firm and dry surface.

4.0 RESULTS AND DISCUSSION

The time-distance curves for each location are shown on Figure 3. Most curves are close to straight lines passing through the origin and give a good estimate of the seismic velocity. In some cases (e.g. G3W), however, the time-distance curves are more complex and appear to comprise of two components. Near the geophone, first arrival times tend to follow a straight line (e.g. 7,500 ft/sec. for G3W), while the points further from the geophone appear to indicate a lower velocity (e.g. 4,750 ft/sec. for G3W - Figure 3). Such a feature could be caused by one of two possible situations. Firstly, there may be a lateral change in the seismic velocity of the gypsum (see Figure 2b). This would be the case if,for example, the material further from the geophone were softer than that in its immediate vicinity. Alternatively, increasing attenuation of the seismic energy with increasing distance from the geophone may mean that the time measured at the geophone was not a true first arrival. This would result in an apparent velocity lower than the true velocity. In most cases, however, the straight line portion close to the geophone is well established and is used as an estimate of the seismic velocity at a particular geophone location and for the chosen orientation.

The seismic velocities of the synthetic gypsum on December 20 were found to range from 4,500 to 7,500 ft/sec., with an overall average of 6,160 ft/sec. (see Table 1). No marked differences were found for seismic velocities in different directions.

By January 10, 1980 the seismic velocity had increased at all locations by approximately 2,000 ft/sec. Velocities were found to range between 6,900 and 9,500 ft/sec with an average value of 8,115 ft/sec. Once again, there was no apparent difference in the seismic velocities for different orientations.

The significant increase in seismic velocities at all stations (Figure 3) over a period of three weeks indicates that given more time for the synthetic gypsum to consolidate further, velocities would approach those values found in previous surveys (i.e. in the order of 10,000 ft/sec.).

Following the second survey, attempts were made by Allied Chemical Canada Ltd. to "rip" some of the waste material. It was discovered that although the surface gypsum was generally fairly hard and platey, at depth the material appeared less consolidated. This emphasizes an important point about seismic velocity determinations which is fundamental in assessing the feasibility of using it as an indicator of rippability for gypsum. In a situation where a hard layer (i.e. higher velocity) overlies a softer one (i.e. lower velocity), it is not possible to determine the velocity of the second layer from the time-distance curve (see Figure 2c). Only if the upper layer overlies a layer with a higher seismic velocity is it possible to estimate the latter velocity from the time-distance curve (see Figure 2d). This is a severe limitation in the use of surface seismic measurements for the determination of overall hardness in the early stages of consolidation of synthetic gypsum.

5.0 CONCLUSIONS AND RECOMMENDATIONS

The results of this survey show that the seismic velocity of synthetic gypsum increases during hardening, but due to the physics of the seismic waves in layered media it is only possible to determine the vertical seismic velocity profile if those velocities increase with depth. This is unlikely to be the case in the gypsum waste pond therefore the subsurface layer may still be in an inappropriate condition for removal even though the seismic velocities indicate otherwise. It may be preferable therefore to test the gypsum directly using for example, auger techniques.

GOLDER ASSOCIATES
J.M. Boyd
for Peter A. Smith

REGISTERED PROFESSIONAL ENGINEER
J. M. BOYD
PROVINCE OF ONTARIO

PAS:hs
791-1372

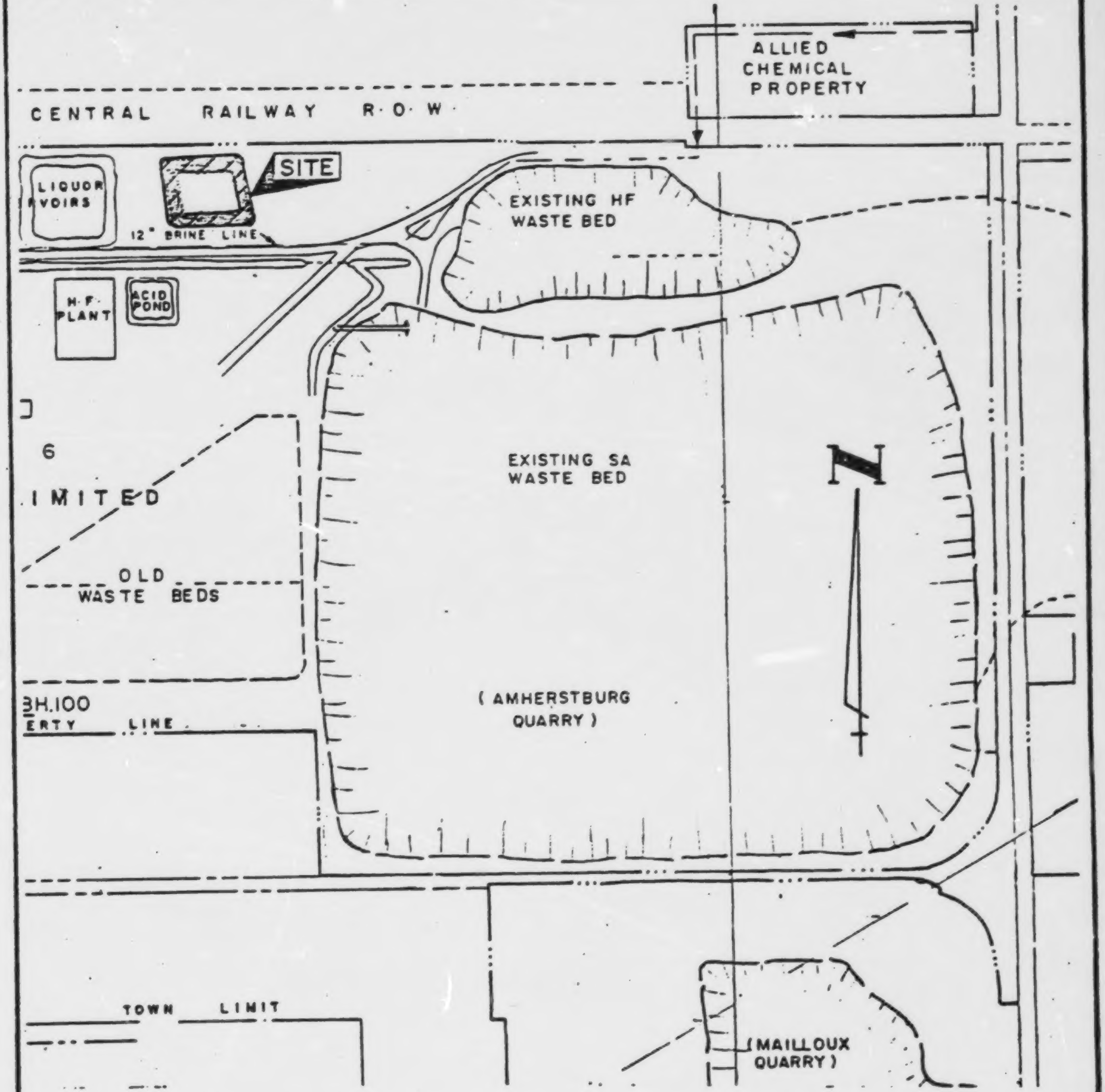
TABLE 1

SEISMIC VELOCITIES OF THE SYNTHETIC GYPSUM

STATION	DIRECTION	VELOCITY (ft/sec.) Dec. 20/79	Jan. 10/80	Change
G1	N-S	7,500	9,500	+2,000
	E-W	7,300	8,500	1,200
G2	N-S	5,750	7,000	1,250
	E-W	4,750	7,000	2,250
G3	N-S	6,100	7,150	1,050
	E-W	7,500	8,300	800
G4	N-S	5,000	8,250	3,250
	E-W	4,500	6,900	2,400
G5	N-S	5,700	9,500	3,800
	E-W	7,500	9,050	1,550
Averages	N-S	6,010	8,280	2,270
	E-W	6,310	7,950	1,640
	Overall	6,160	8,115	1,955
	Standard Deviations	1,210	1,043	

SITE LOCATION PLAN

FIGURE 1



ALLIED CHEMICAL PROPERTY
CENTRAL RAILWAY R.O.W.
SITE
LIQUOR RVOIRS
12" BRINE LINE
EXISTING HF WASTE BED
H.F. PLANT
ACID POND
6
IMITED
OLD WASTE BEDS
EXISTING SA WASTE BED
(AMHERSTBURG QUARRY)
N
BH.100
ERTY LINE
TOWN LIMIT
(MAILLOUX QUARRY)

SCALE : 1 TO 7200

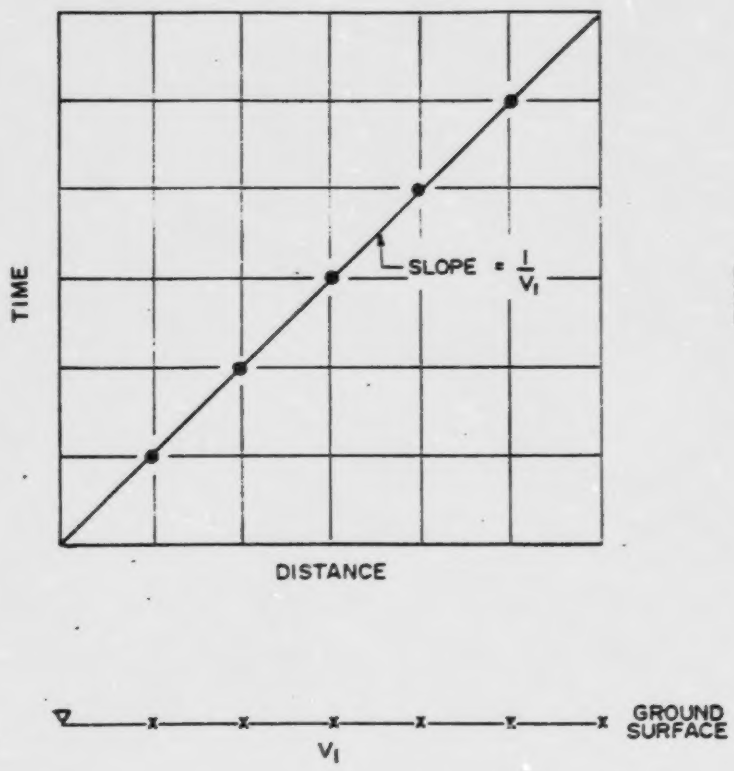
Date MARCH 25,1980

Project 791-1372

Golder Associates

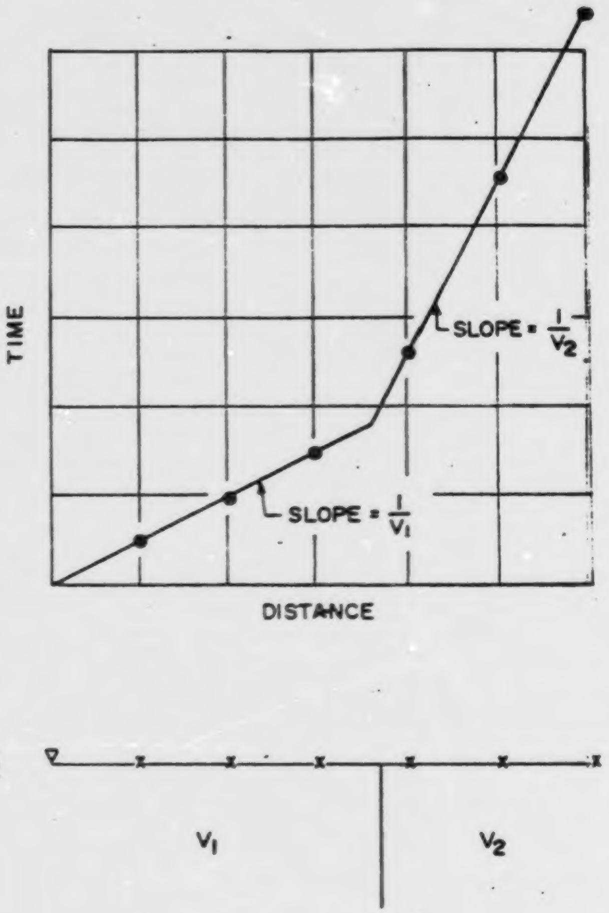
Drawn E.F.O.

Chkd. P.A.S.



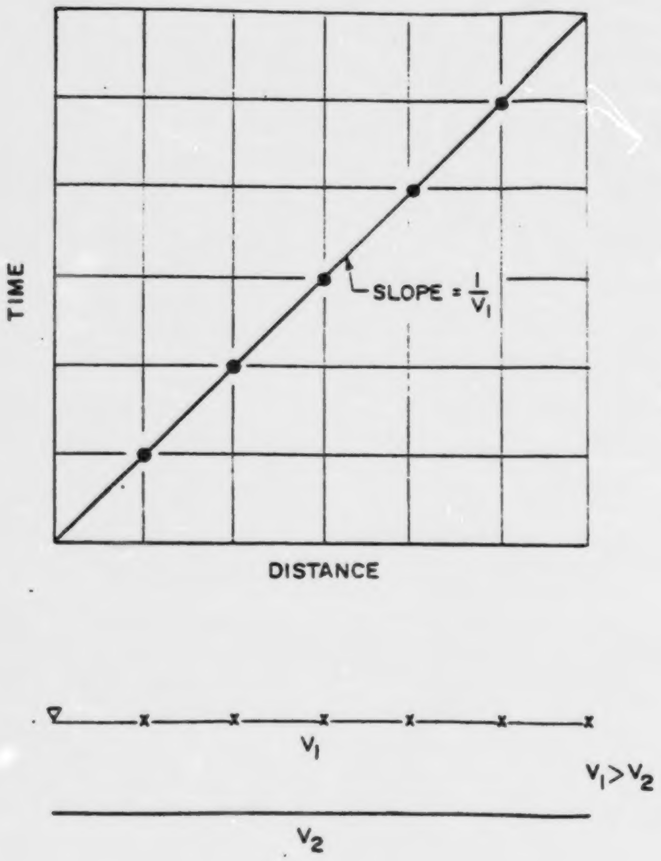
(A)

SINGLE LAYER, VELOCITY = V_1



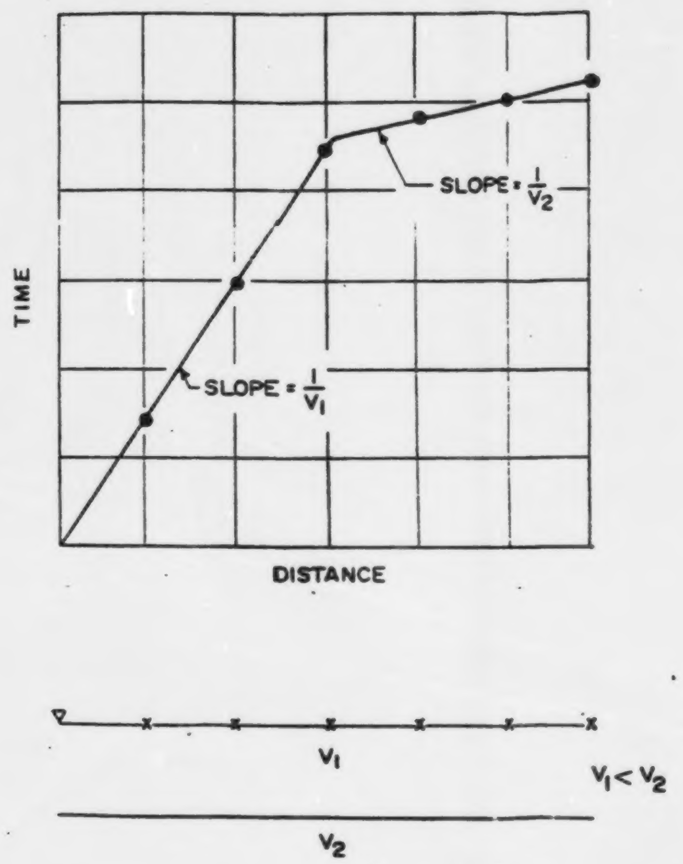
(B)

LATERAL CHANGE IN VELOCITY, $V_1 > V_2$



(C)

HIGH VELOCITY SURFACE LAYER OVERLYING LOWER VELOCITY LAYER
N.B. LOWER LAYER NOT DETECTED ON TIME – DISTANCE CURVE



(D)

LOWER VELOCITY LAYER AT SURFACE
N.B. LOWER LAYER IS REPRESENTED ON TIME – DISTANCE CURVE

T

LEGE
x HAMM
▽ GEOR

Date MARCH

Project 791-13

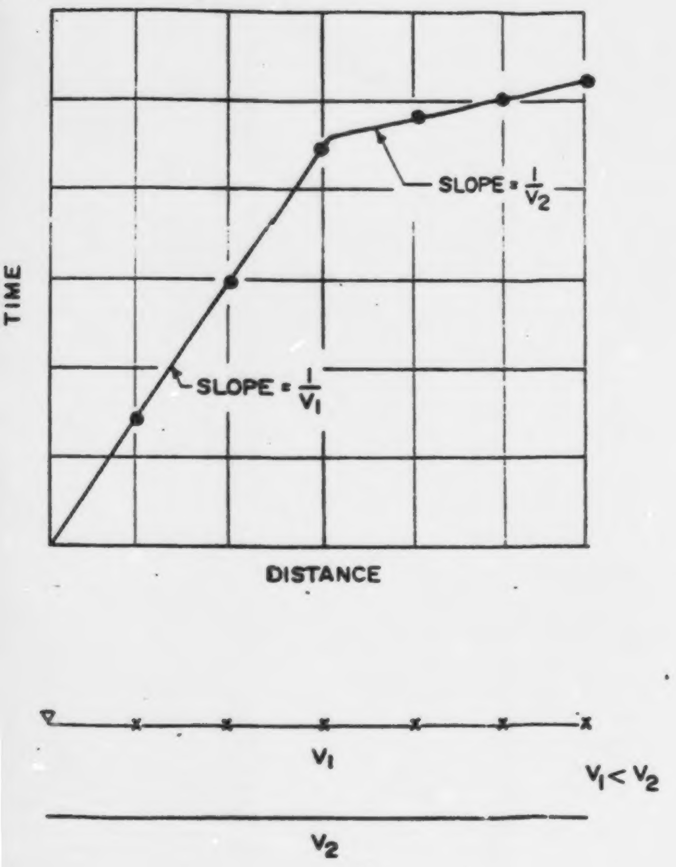
TYPICAL TIME - DISTANCE CURVES

FIGURE 2

LEGEND

x HAMMER POINTS

▽ GEOPHONE


TIME
SLOPE = $\frac{1}{V_2}$
SLOPE = $\frac{1}{V_1}$
DISTANCE
V_1
$V_1 < V_2$
V_2

(D)

LOWER VELOCITY LAYER AT SURFACE

N.B. LOWER LAYER IS REPRESENTED ON TIME - DISTANCE CURVE

Date MARCH 25, 1980

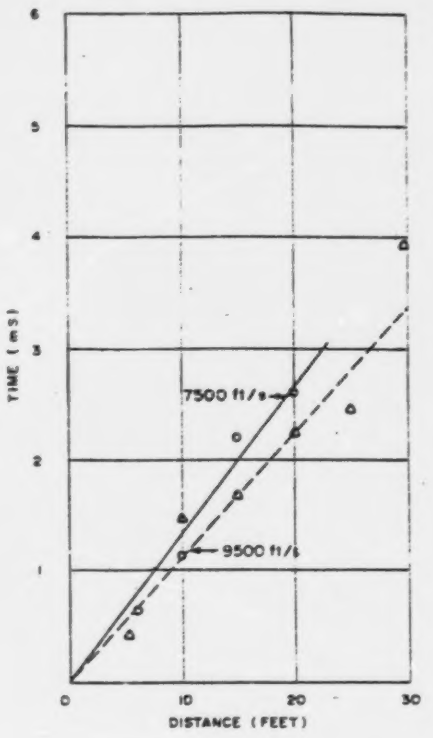
Project 791 - 1372

Golder Associates

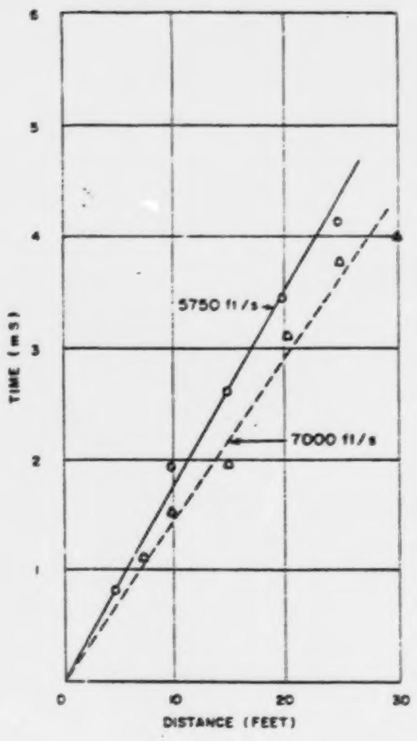
Drawn RL

Chkd

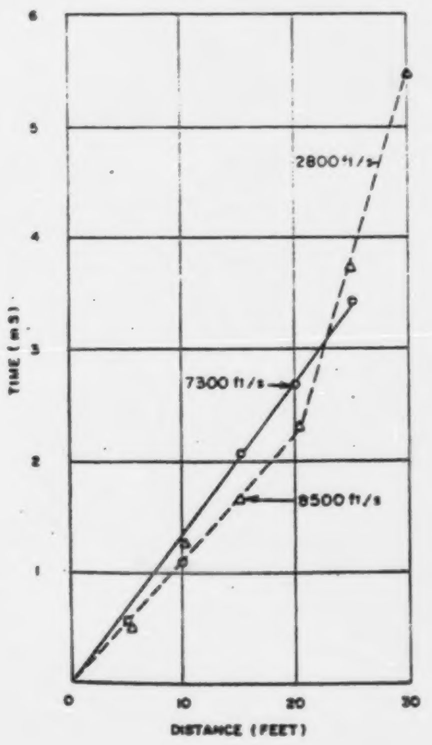
G1(N)



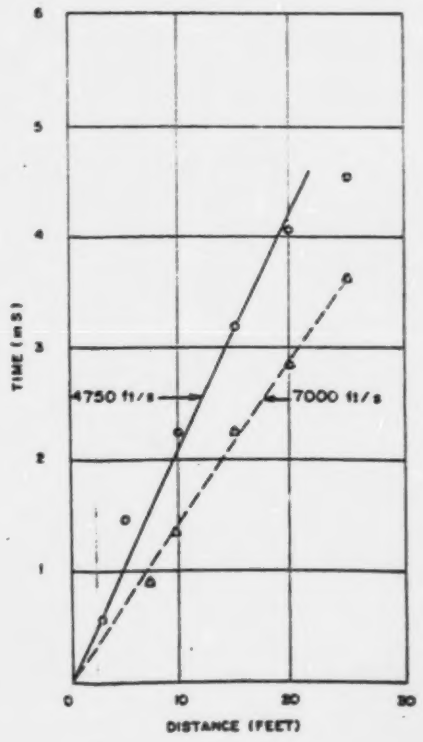
G2(N)



G1(E)



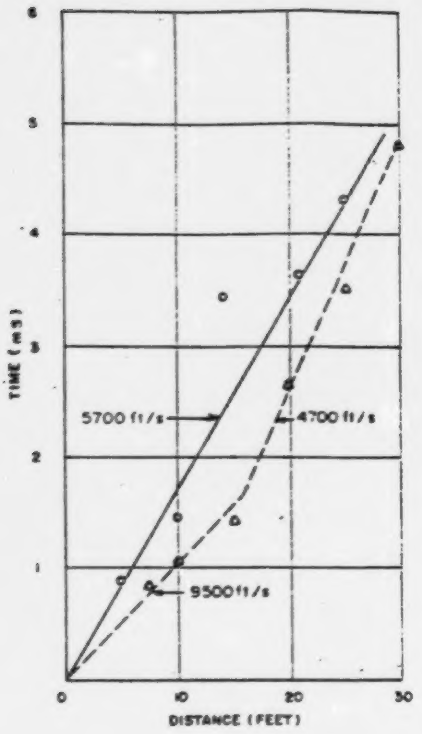
G2(E)



TIME-DISTANCE CURVES FOR SURVEYS

FIGURE 3

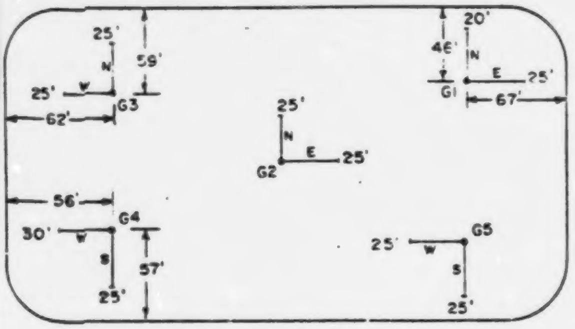
G5(S)



LEGEND

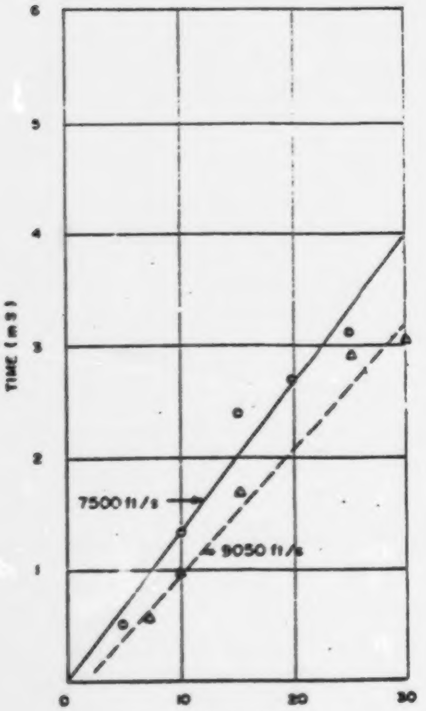
○——○ TIME-DISTANCE CURVES FOR DECEMBER 20, 1978

△ - - △ TIME-DISTANCE CURVES FOR JANUARY 10, 1980


25'
N
59'
25'
W
G3
62'
20'
46'
N
G1
E
25'
67'
25'
N
G2
E
25'
56'
G4
30'
W
S
57'
25'
25'
W
G5
S
25'

LOCATION OF LINES
(NOT TO SCALE)

G5(W)



Date MARCH 25, 1980
Project 791-1378

Golder Associates

Drawn
Chkd

ATTACHMENT B

ORF - SUMMARY REPORT "TECHNIQUES
FOR SOLIDIFICATION OF FLUOROANHYDRITE"

DEPARTMENT OF MATERIALS CHEMISTRY

SUMMARY REPORT

TECHNIQUES FOR SOLIDIFICATION OF FLUOROANHYDRITE

for

Allied Chemical Canada Limited
201 City Centre Drive
Mississauga, Ontario
L5B 2T4

Attention: Mr. R.V. Aitken, Manager
Business Development

Prepared by:

L.M. Luckevich
August 30, 1982

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FOUNDATION

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SUMMARY

Problems were encountered in the utilization of Allied fluorogypsum, a by-product of hydrofluoric acid manufacture, in cement manufacture because of fluorogypsum inhomogeneity. The inhomogeneity was attributed to regions of inert, non-gypsum fines introduced in the neutralization of the kiln effluent (fluoroanhydrite) prior to hydration to fluorogypsum. It was determined that cyclone removal of the fines yielded a coarse material possessing uniformly adequate hardening/hydration properties. A hydrocyclone was installed into the fluoroanhydrite process stream. Testing of the underflow (coarse) and overflow (fines) ponds showed the underflow solids to be acceptable, after a suitable hydration period (~6 weeks) for use in cement manufacture. This was true also after the material had been subjected to freeze-thaw cycling. The overflow solids were considered not acceptable for use in cement manufacture. The yield of acceptable material was dependent on the initial particle size distribution of the kiln effluent, which fluctuates substantially. Maximum yield is estimated to be 67%.

1. INTRODUCTION

In 1980, Allied Chemical Canada Limited (ACCL) undertook a program to investigate the use of by-product calcium sulphate (fluoroanhydrite), from HF manufacture, as a set control agent in Portland cement. Preliminary testing conducted at the St. Lawrence Cement Co., used material harvested directly from the residue storage area and yielded promising results. Subsequent testing, again using material harvested directly from the residue storage area, showed the material was not acceptable. It was obvious that the residue was not homogeneous and that some portions were not acceptable for use in cement manufacture.

Calcium sulphate compounds are used in Portland cement to control the rate at which the cement paste develops strength at the early ages and to control the shrinkage of the cement products during drying. Approximately two to five percent calcium sulphate is added by intergrinding it with the cement clinker. In order that good grinding conditions be maintained, the calcium sulphate should be added primarily in lump form. A finely-powdered product is not acceptable. The unacceptable portion of ACCL by-product calcium sulphate was a moist, finely-powdered product while the acceptable portion was a hard rock-like product.

The Ontario Research Foundation (ORF) was approached by ACCL in June, 1980 for assistance in elucidating the cause of the pond inhomogeneity and in determining techniques for producing a uniformly acceptable by-product calcium sulphate. This report is a summary of work performed by ORF on behalf of ACCL.

2. LABORATORY WORK

2.1 Background

The initial laboratory work comprised sedimentation, hydration and strength tests of neutralized and unneutralized fluoroanhydrite slurries. Observations were that:

- the unneutralized slurry solids settled quickly to a dense sediment which hardened uniformly to a hard rock-like mass. All of the material was calcium sulphate.
- the neutralized slurry solids settled more slowly to a sediment with two distinct layers. The coarser material was 100% fluoroanhydrite that hydrated to a hard rock-like mass. The finer material was a mixture of fluoroanhydrite and other inert solids, these being introduced via the neutralizing medium, brine muds. The finer material did not develop strength upon hydration to fluorogypsum.

It was thus determined that the fluorogypsum in the residue storage area was inhomogeneous with respect to strength because of the presence of fine brine muds solids which, through particle size classification upon settling, were concentrated into a single layer of the sediment. If the brine muds solids could be either removed or distributed uniformly throughout the sediment, the material would be homogeneous and of acceptable strength.

The initial approach taken by ORF investigated the uniform distribution of the fine fraction throughout the coarser particles using surface active agents. This was unsuccessful.

The second approach taken by ORF investigated removal of the fine fraction of the neutralized slurry solids by a hydrocyclone. The remainder of the ORF work addressed the following tasks:

- laboratory simulation of the action of a hydrocyclone on the neutralized fluoroanhydrite slurry; characterization and evaluation of the simulated hydrocyclone effluents.
- characterization and evaluation of the actual hydrocyclone effluents.
- characterization and evaluation of the hydrocyclone residue storage areas.

2.2 Laboratory Simulation of Hydrocyclone Effluents

To simulate the action of a hydrocyclone on the neutralized fluroanhydrite slurry (five percent anhydrite solids in recycle water, neutralized to pH 5 using brine muds), the slurry was poured through a 230 mesh (63 micron) sieve. The material retained on the sieve was dried and weighed; it was 65 percent (by weight) of the total amount of solids added. The dried solids were reslurried with the mother liquor (decanted from the fine fraction) at a solids content of 40 percent. The coarse fraction slurry represented the hydrocyclone underflow; the fine fraction slurry (solids - 63 microns) represented the hydrocyclone overflow.

The following properties of the simulated hydrocyclone measured:

- composition
- rate of solids strength development
- rate of fluoroanhydrite hydration

2.2.1 Composition of Simulated Hydrocyclone Effluents

The simulated hydrocyclone overflow was 1.5 percent solids of which approximately 88 percent was anhydrite and 12 percent was brine muds solids. The simulated hydrocyclone underflow (coarse fraction) solids were 97 percent anhydrite and 3 percent brine muds solids. The yield of the underflow was 67 percent, i.e. 67 percent of the anhydrite originally added was present in the coarse particle size fraction and 33 percent of the anhydrite solids were smaller than 63 microns.

The sediment density for the coarse material was about 1.8 g/cc and for the fines about 0.3 g/cc. Thus, for a certain weight of fluoroanhydrite effluent, the underflow (67 percent fluoroanhydrite yield) represented about 25 percent of the total volume and the overflow, about 75% of the total volume.

X-ray diffraction showed the brine muds solids to be composed of calcium carbonate ($CaCO_3$) and sodium chloride ($NaCl$). These compounds were also present in both the coarse and the fine material.

2.2.2 Rate of Solids Strength Development

The wet strength of the simulated effluent sediments was measured after 1, 2, 3, and 4 weeks elapsed time using an Instron mechanical testing device fitted with a needle-like probe. The simulated underflow solids had breaking loads greater than $\sim$100 lbs. (average of at least five trials) whereas the simulated overflow solids showed no strength development and gave no measurable resistance to the testing device.

2.2.3 Rate of Conversion to Gypsum

The rate of conversion to gypsum of the coarse and fine fraction solids was measured. After seven days hydration time, the fine fraction was ~90% gypsum and hydration was complete. (The fine fraction solids were 10% brine muds solids). After seven days hydration time, the coarse material was ~43% gypsum and by 28 days it was ~57% gypsum.

2.2.4 Conclusions of Hydrocyclone Simulation

It was concluded from the laboratory simulation of hydrocyclone effluents that a separation technique based on particle size would yield a coarse (+63 micron) fraction possessing uniformly good hardening properties at a fluoroanhydrite yield of 67 percent. The fine (-63 micron) fraction would comprise the majority of the slurry volume (~75%) and would not have good hardening properties even though it was predominantly anhydrite which hydrated rapidly.

An investigation was performed into utilization of the overflow via circulation until hydration was complete (several days), then followed by gypsum harvest. The circulation volume required for this was considered by ACCL to be prohibitively large.

The results obtained from the laboratory hydrocyclone simulation indicated that installation of a hydrocyclone into the fluoroanhydrite process stream would yield a coarse fraction which solidified uniformly to a product acceptable for use in cement manufacture. By September 1981, ACCL had installed a hydrocyclone at the Amherstburg Plant and built test ponds to contain the effluents.

2.3 Characterization and Evaluation of Hydrocyclone Effluents

The hydrocyclone was installed into the fluoroanhydrite process stream and hydrocyclone effluent samples were collected by ORF personnel. On the first sampling date (September 23, 1981), the plant kiln was operating at approximately half capacity and the fluoroanhydrite by-product was markedly different from that previously tested at ORF, the major differences being a much whiter colour and that no pebble-size particles were observed. On the second sampling date (November 16, 1981), the plant kiln was operating at approximately 90% capacity and the effluent appeared somewhat coarser but still did not contain the ~1-inch pebbles present in the material used in the laboratory simulation of the effluents.

The following samples were collected from the hydrocyclone installation:

September 23	November 16
• overflow slurry	• overflow slurry
• overflow pond solids	
• underflow slurry	• underflow slurry
• underflow pond solids	

The underflow pond solids were different from the underflow slurry solids in that a small bleed stream of the unseparated slurry was used to assist the flow of the underflow slurry into the pond, resulting in unseparated slurry solids being added to the underflow pond solids.

The effluent samples were characterized according to composition, pH, particle size distribution, chloride content and hydration rate; underflow solids only were tested for strength development and durability.

2.3.1 Effluent Composition and pH

The pH of all effluent samples was measured; all samples were neutral (pH = 7).

The solids composition was determined using X-ray diffraction. The solids were filtered if necessary, then dried and ground before analysis.

The X-ray diffraction showed the underflow slurry solids from both collection dates to be composed of anhydrite and gypsum only and the overflow slurry solids from both collection dates to be composed mainly of gypsum and anhydrite with a small proportion of calcite ($CaCO_3$). The underflow pond solids were composed mainly of gypsum and anhydrite with small amounts of lime (($Ca(OH)_2$) and calcite ($CaCO_3$). The low concentration of solid impurities in the underflow pond (lime and calcite) were most likely introduced to the underflow pond via the unseparated slurry bleed stream.

2.3.2 Solids Content and Particle Size Distribution

The solids content and particle size distribution of the overflow slurry, overflow pond, underflow slurry and underflow pond were measured; data being given in Table I and Figures 1 - 4. The data show that the hydrocyclone was giving good separation at the particle size desired. Both effluents had higher solids content on the second collection date with the solids being coarser i.e. the underflow solids had a coarser particle size distribution on the second collection date. The hydrocyclone yield was not calculated; however, it appeared from the fineness of the solids that the yield was less than that predicted (~67%) based on the laboratory simulation.

2.3.3 Chloride Content

The maximum allowable level of soluble chloride in gypsum for use in cement is 1%. The chloride level of the liquids and solids from the underflow and overflow were measured. The solids were well below 1% as shown in Table III. All of the liquid samples contained approximately 1% chloride but because this liquid is drained from the ponds, increased chloride concentration via evaporation is not expected to be a problem.

2.3.4 Hydration Rate

The hydration rate of fluoroanhydrite to fluorogypsum was measured for the underflow slurry solids, underflow pond solids and overflow pond solids; data being given in Figure 5. In the case of the overflow, the majority of the conversion (to 55% gypsum) occurs in the first two weeks whereas it takes the underflow solids 3 - 4 weeks to reach the same level of hydration. After this time, the rate slows considerably and conversion of the remaining anhydrite occurs very gradually. Thus, 4 - 6 weeks after placement of the hydrocyclone underflow would be sufficient time for significant hydration to occur.

2.3.5 Compressive Strength

The hydrocyclone underflow solids were cast into 2" cubes and cured under water. Samples were removed at intervals of one week, dried, and the compressive strength was measured. The compressive strength development curves are shown in Figure 6.

The second batch of fluoroanhydrite showed very rapid initial strength development. At one week, the compressive strength of the material was three times that of the first batch at seven weeks ($\sim$3000 psi cf 1000 psi). The compressive strength of the second batch of fluoroanhydrite continued to increase to a final value of $\sim$5500 psi at three weeks. Both materials have sufficient strength to be used in cement manufacture.

2.3.6 Durability (Resistance to Freeze-Thaw)

The hydrocyclone underflow solids from the first collection date were cast into 3" x 3" x 15" prisms, cured for six weeks and subjected to repeated cycles of freezing and thawing in water according to ASTM C666, Procedure A. After five freeze-thaw cycles, the fluorogypsum was cracked and broken and the compressive strength could not be measured; after four weeks further curing, several of these cracks had healed over and the strength of the material was increasing.

The material had poor durability. However, the conditions of the test method were more severe than those which would be experienced in the pond and it was impossible to predict if the milder freeze-thaw conditions of the pond would indeed be as detrimental to the material.

2.4 Characterization and Evaluation of Hydrocyclone Residue Storage Areas

Six core samples (2½ inch diameter) from the hydrocyclone underflow test pond and two core samples from the hydrocyclone overflow test pond were procured from the Allied fluorogypsum test ponds as demonstrated by Figure 7. Samples are labelled Coarse A - Coarse F and Fine A - Fine B. Samples Coarse F, Fine A and Fine B had undergone several weeks of below freezing temperatures as well as approximately two weeks of freeze-thaw temperatures. The samples were transported to the Ontario Research Foundation for testing; they were kept wet at all times. Samples Coarse A - Coarse E were collected in December 1981; all other samples were collected in February 1982.

Six centimetre (2½ inch) length samples were cut at various positions along the core and tested for:

- gypsum content
- unconfined compressive strength
- chloride content of contact water
- chloride content of leached water
- permeability (falling head)

The chloride content of the gypsum in Coarse F, Fine A and Fine B was also measured.

2.4.1 Gypsum Content

Samples procured from various positions along the cores were dried, ground and calcined at 360°C. The weight loss upon calcination was measured and used to calculate the proportion of gypsum. The data (Figure 8) show that the gypsum content fluctuates between 30% and 85% throughout the coarse pile and between 60% and 80% throughout the fines pile. No trends were observed with respect to distance from surface or position in pile except with Coarse A which was composed of both recently deposited (Fall 1981) material and previously deposited (Summer 1981) material.

The material at the very bottom of this core was much coarser (when deposited) than that deposited more recently and thus less reactive surface area per unit weight was available for hydration. The gypsum content of this coarser material is generally lower than that of all other samples (∿40%).

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It is recommended* that when gypsum/anhydrite blends are used as set control agents in Portland cement that the blend should contain 40 - 60% of its SO_3 in the gypsum and 60 - 40% of its SO_3 in the anhydrite. This corresponds to an average fluoroanhydrite conversion of 45 - 65% gypsum. The average gypsum contents of the core samples range from 50 - 58% gypsum and satisfy this criterion.

2.4.2 Permeability

The permeability of the samples was measured in a triaxial compression chamber using a falling head permeameter. The data (Table IV) show that the coarse pond material ranges in permeability from a high of 10^{-3} cm/s (one sample only) to a low of 10^{-6} cm/s. Most samples are in the 10^{-5} cm/s to 10^{-6} cm/s range. The fines pond material ranges in permeability from a high of 10^{-3} cm/s to a low of 10^{-5} cm/s with most samples being in the 10^{-3} to 10^{-4} cm/s range.

Thus, the coarse pond material can be considered impermeable. This means that rainfall will tend to drain off the surface and that the chloride content of the solids will not fluctuate significantly once equilibrium is reached. The chloride content of the underflow solids (when dried) is typically 0.1 - 0.3%. The maximum permissible is 1%. The chloride content of the gypsum/anhydrite blend will almost always be within this range, regardless of when the material is harvested.

The fines pond is much more permeable than the coarse pond and its capacity for releasing chloride into the environment is correspondingly greater. The chloride content of the fines pond solids will thus decrease over time as water percolates through the pile and washes chloride away.

---

*Gypsum and Anhydrite in Portland Cement, 2nd Edition, W.C. Hansen and J.S. Offut, United States Gypsum, 1969.

2.4.3 Gypsum Chloride Content

The chloride concentration in dried, ground samples at various positions along Coarse F, Fine A and Fine B was measured, average values being given in Table V. In the fines pond, the chloride content of the material ranges from 0.10 to 0.36% by weight and in the coarse pond, the chloride content of the material ranges from 0.15 to 0.39% by weight. Thus, the coarse pond solids have slightly higher chloride than those in the fines pond. This is likely due to the higher permeability of the fines pond resulting in greater chloride leaching rates from the solids. All chloride levels are well below the maximum of 1% stipulated by the cement industry.

2.4.4 Liquid Chloride Content

The soluble chloride concentration of the liquid in which the cut core samples were soaking and of the liquid leached through the core samples during permeability testing was measured, average values being given in Table V. The data indicate that the chloride levels in the coarse pond liquid samples range from a low of 0.0024% (24 ppm) to a high of 0.5525% (5,525 ppm). The chloride levels in the fines pond liquid samples range from 0.1103% (1,103 ppm) to 0.3578% (3,578 ppm). Thus, the chloride content of the liquid which will leach from the ponds will be in the 1,000 to 4,000 ppm range.

2.4.5 Compressive Strength

The compressive strength of the samples was measured at various positions along the core. The samples were tested moist and uncapped; maximum load was reached in approximately one minute. The data (Figure 10) show that the average strength of all of the coarse pond samples is very high (900 - 1200 psi) but that a region of lower strength is observed in all of the samples 2 - 3 feet below the surface. This region has a compressive strength of 300 - 600 psi. In the fines pond (Figure 10), the material is generally low in compressive strength (200 - 400 psi). One exception occurs at the bottom of the pile in Fine A, where the compressive strength is 1,125 psi. This is the same region where exceptionally high permeability is observed and it is probable that this material originated not from the hydrocyclone overflow solids but from previous disposition.

Although the coarse pond was not homogeneous with respect to compressive strength, all regions had the minimum compressive strength required and the material was considered acceptable for use in cement manufacture. The fines pond material was considered unacceptable.

3. DISCUSSION AND CONCLUSIONS

The project performed at ORF on behalf of ACCL elucidated the source of fluorogypsum inhomogeneity in the residue storage area. The inhomogeneity is caused by layering of the coarser fluoroanhydrite and finer, inert material introduced by the neutralizing medium, brine muds. Analysis of the material produced by the kilns from Fall 1980 to Spring 1981, (including a hydrocyclone simulation) showed that separation of the fine and coarse material at 63 micrometers yielded a coarse fraction which was almost 100% anhydrite and which solidified uniformly into a rock-like mass; yield of fluoroanhydrite in the coarse material was measured at 67%. A hydrocyclone was selected for installation into the fluoroanhydrite process stream using particle size data and flow rates existing at that time.

The hydrocyclone was installed and in September 1981, samples were collected by ORF personnel. Analysis of the effluents showed:

(a) the particle size distribution of the unseparated slurry solids to be much finer than that previously observed, resulting in a lower underflow yield, and,

(b) the hydrocyclone underflow solids were considered uniformly acceptable for use in cement manufacture after an elapsed hydration time of six to eight weeks.

A second series of samples was collected in November 1981; analysis of the effluents showed:

(a) the particle size distribution of the unseparated slurry to be coarser than that of the previous sample yet still finer than that upon which hydrocyclone selection was based, and,

(b) the hydrocyclone underflow solids were considered uniformly acceptable for use in cement manufacture after an elapsed hydration time of four to six weeks.

Core samples were procured from the underflow test ponds in December 1981 and tested for gypsum content, strength, soluble chloride and permeability. It was concluded that even though the pile was not homogeneous the material was uniformly acceptable for use in cement manufacture when harvested in depths of five to seven feet, (the core sample depth). One more core sample was taken in February 1982 after the ponds had been subjected to several weeks of below freezing temperatures as well as approximately two weeks of freeze-thaw temperatures. This core sample had comparable properties to the earlier samples and it was concluded that the freeze-thaw cycling to which the fluorogypsum had been exposed did not detrimentally affect its properties.

Core samples were procured from the overflow test ponds, also in February 1982, and tested for gypsum content, strength, soluble chloride and permeability. The fines pond material, even though it was predominantly gypsum (~72%) had significantly lower strength and higher permeability than the coarse pond material and was characterized as being not suitable for use in cement manufacture.

Thus, the conclusion drawn from the project is that a cyclone separation of the fine and coarse material at ~63 micrometres yields a coarse material which is uniformly acceptable in cement manufacture. This conclusion is valid regardless of the original particle size distribution of the fluoroanhydrite slurry. Changes in the particle size distribution of the kiln effluents changes the fluorogypsum quality (with increasing strength as coarseness increases) as well as the hydrocyclone yield (with increasing yield as coarseness increases. However, the hydrocyclone underflow, after a suitable hydration period has elapsed, should always have sufficient strength and thus suitable grinding properties, for use in cement manufacture.

L.M. Luckevich
Associate Research Scientist

for I.H. Joyce
Assistant Director

/gb

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TABLE I

SOLIDS CONTENT OF EFFLUENTS

	September 23	November 16
Overflow	1.7% Solids	10% Solids
Overflow Pond	70.2% Solids	
Underflow	7.6% Solids	34% Solids
Underflow Pond	81.2% Solids	

TABLE II

PARTICLE SIZE DISTRIBUTION OF SOLIDS (SIEVE METHOD)

Sample	Screen Size	% Retained
Underflow	0	18
	44	4
	75	9
	106	20
	149	52
Overflow	0	33
	44	19
	75	10
	106	24
	149	14

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TABLE III

CHLORIDE CONTENT OF HYDROCYCLONE EFFLUENTS

	September 23	November 16
Underflow Liquid	1.07% (w/v)	1.17% (w/v)
Underflow Solids	0.24% (w/w)	0.08% (w/w)
Overflow Liquid	1.12% (w/v)	1.16% (w/v)
Overflow Solids	0.27% (w/w)	0.21% (w/w)

TABLE IV

PERMEABILITY OF CORE SAMPLES

Distance From Surface (feet)	PERMEABILITY (cm/s)							
	COARSE POND						FINES	
	A	B	C	D	E	F	A	B
1	4.78×10^{-6}	1.84×10^{-6} 1.08×10^{-5}	1.13×10^{-5}	1.56×10^{-5}	7.06×10^{-4}	7.22×10^{-5} 3.99×10^{-5} 1.28×10^{-5}	1.48×10^{-3} 2.11×10^{-4} 3.45×10^{-4}	6.52×10^{-4} 2.43×10^{-4}
2			9.16×10^{-6}	4.26×10^{-6}	2.06×10^{-5}	1.81×10^{-3} 8.43×10^{-6}	4.45×10^{-5}	6.21×10^{-3}
3	9.67×10^{-5}	1.08×10^{-4}	3.28×10^{-4}	1.97×10^{-5}	3.58×10^{-5}	2.36×10^{-5} 1.02×10^{-5}		
4	6.38×10^{-5}	1.39×10^{-4}	5.71×10^{-5}	4.37×10^{-5}				
5	8.42×10^{-3}	3.26×10^{-6}	1.13×10^{-5}	4.65×10^{-6}	9.12×10^{-6}			
6	5.00×10^{-4}							

TABLE V

GYPSUM CHLORIDE CONTENT

Sample I.D.	Average Chloride Content (Percent)
Coarse F	0.2905 ± 33%
Fine A	0.2193 ± 47%
Fine B	0.1001 ± 13%

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TABLE VI

LIQUID CHLORIDE CONTENT

Sample I.D.	Average Chloride Content (Soaking Liquid) Percent	Average Chloride Content (Leaching Liquid) Percent
Coarse A	0.0669 ± 30%	0.0451 ± 100%
Coarse B	0.1427 ± 28%	0.1746 ± 57%
Coarse C	0.1043 ± 38%	0.0854 ± 47%
Coarse D	0.1883 ± 37%	0.1653 ± 30%
Coarse E	0.2017 ± 45%	0.1982 ± 20%
Coarse F	0.3998 ± 23%	0.2985 ± 25%
Fine A	0.3029 ± 15%	0.1760 ± 40%
Fine B	0.2896 ± 10%	0.1240 ± 26%

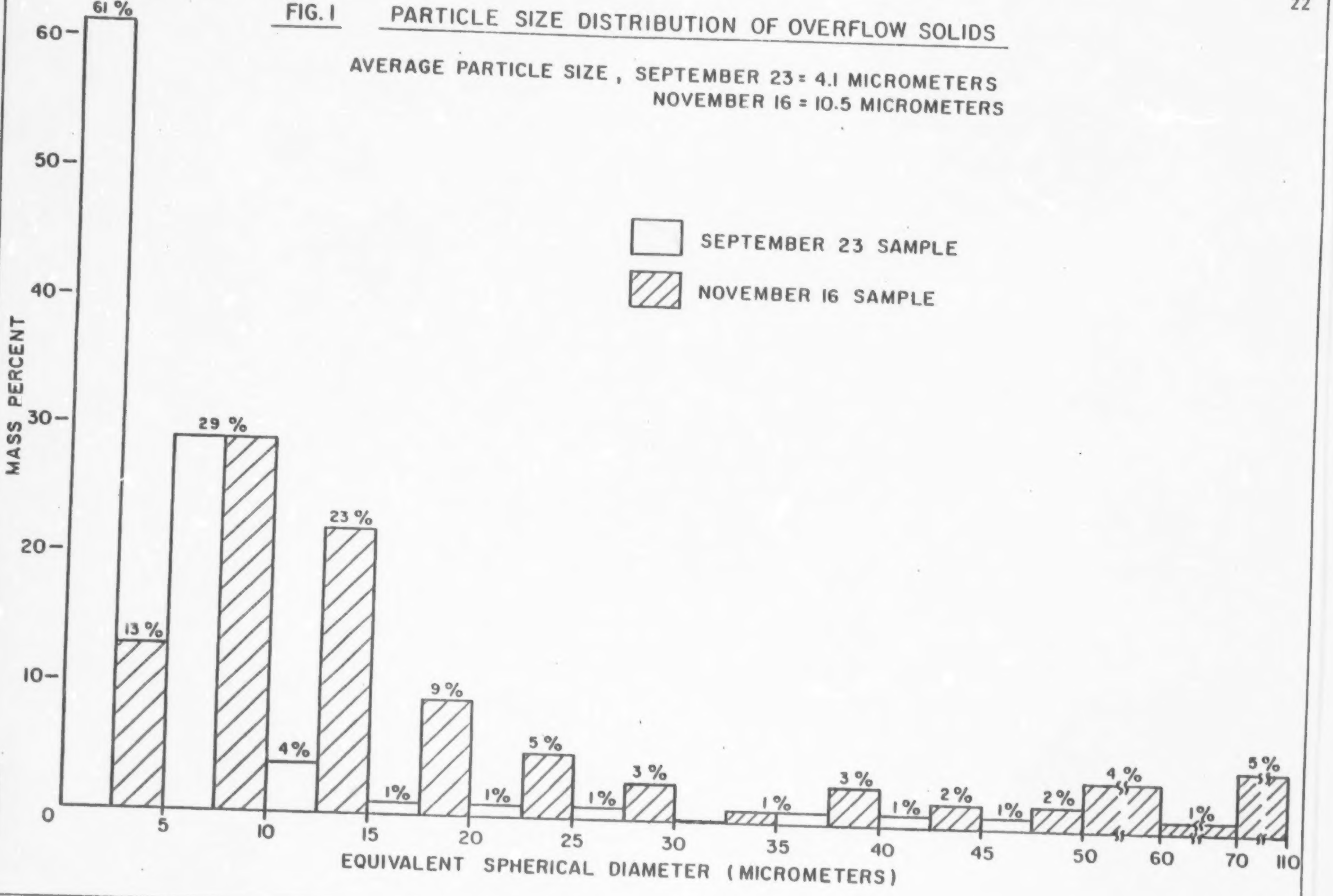


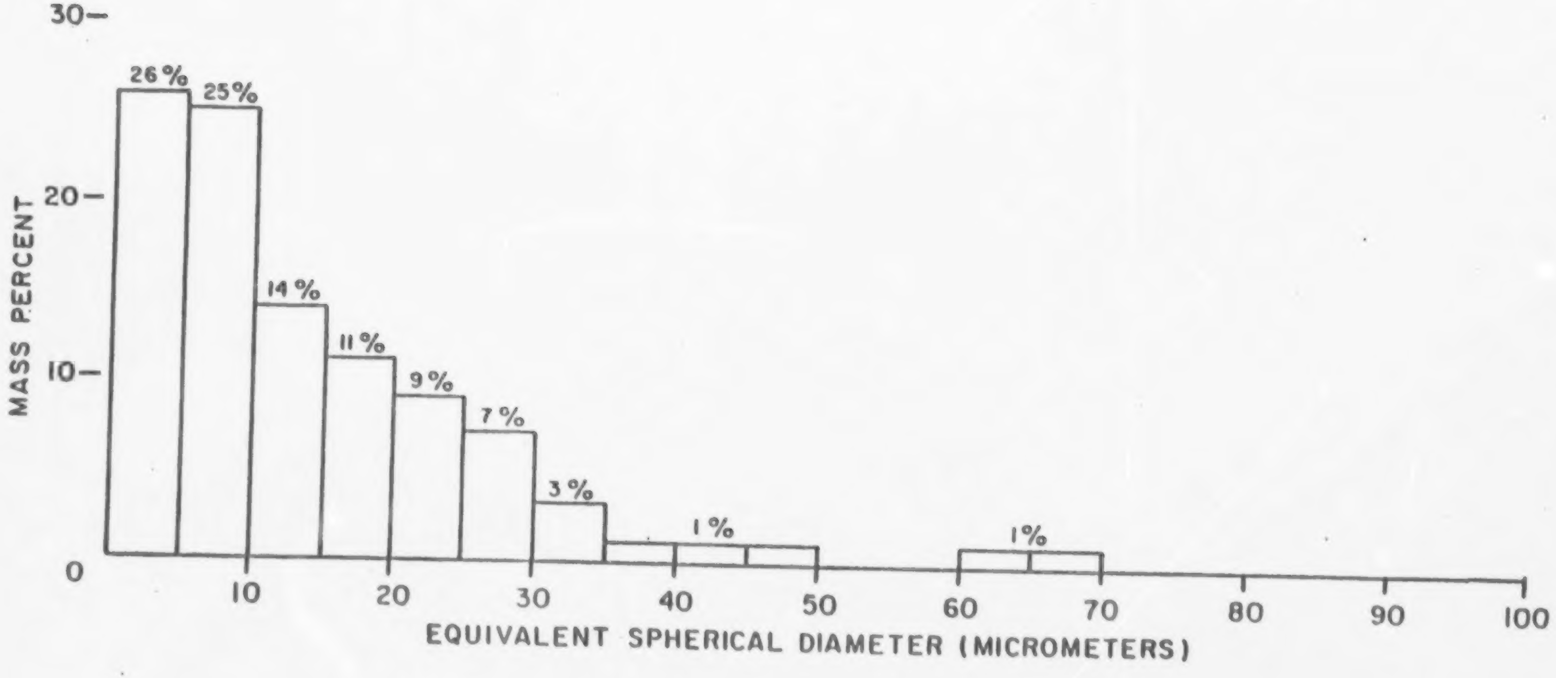
FIG. I PARTICLE SIZE DISTRIBUTION OF OVERFLOW SOLIDS

AVERAGE PARTICLE SIZE, SEPTEMBER 23 = 4.1 MICROMETERS
NOVEMBER 16 = 10.5 MICROMETERS

FIG. 2 PARTICLE SIZE DISTRIBUTION OF OVERFLOW POND SOLIDS

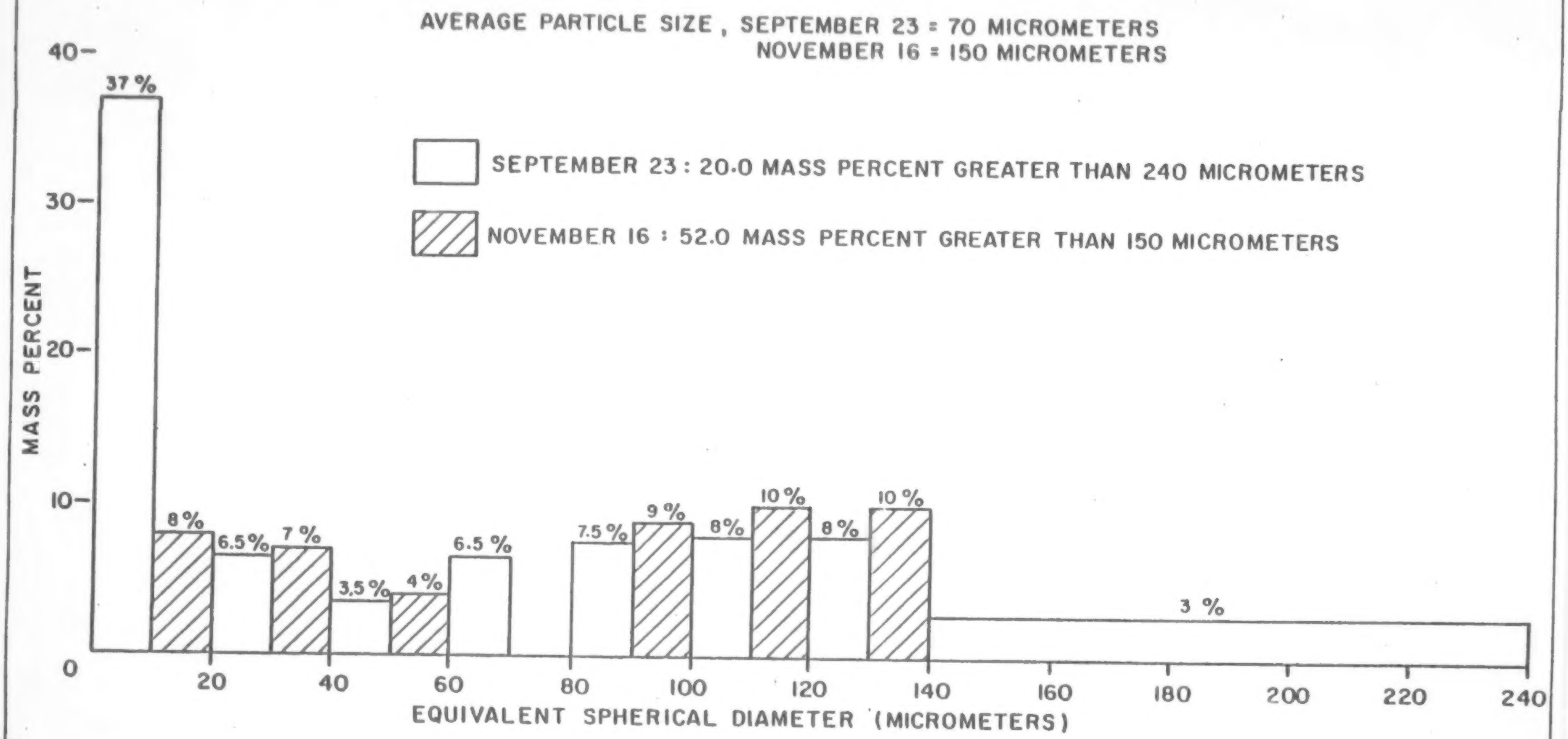
AVERAGE PARTICLE SIZE = 9.5 MICROMETERS

(SEPTEMBER 23 SAMPLE)



ORF

FIG. 3 PARTICLE SIZE DISTRIBUTION OF UNDERFLOW SOLIDS



AVERAGE PARTICLE SIZE, SEPTEMBER 23 = 70 MICROMETERS
NOVEMBER 16 = 150 MICROMETERS

FIG. 4 PARTICLE SIZE DISTRIBUTION OF UNDERFLOW POND SOLIDS

AVERAGE PARTICLE SIZE = 100 MICRONS

27.0 MASS PERCENT GREATER THAN 240 MICROMETERS

(SEPTEMBER 23 SAMPLE)

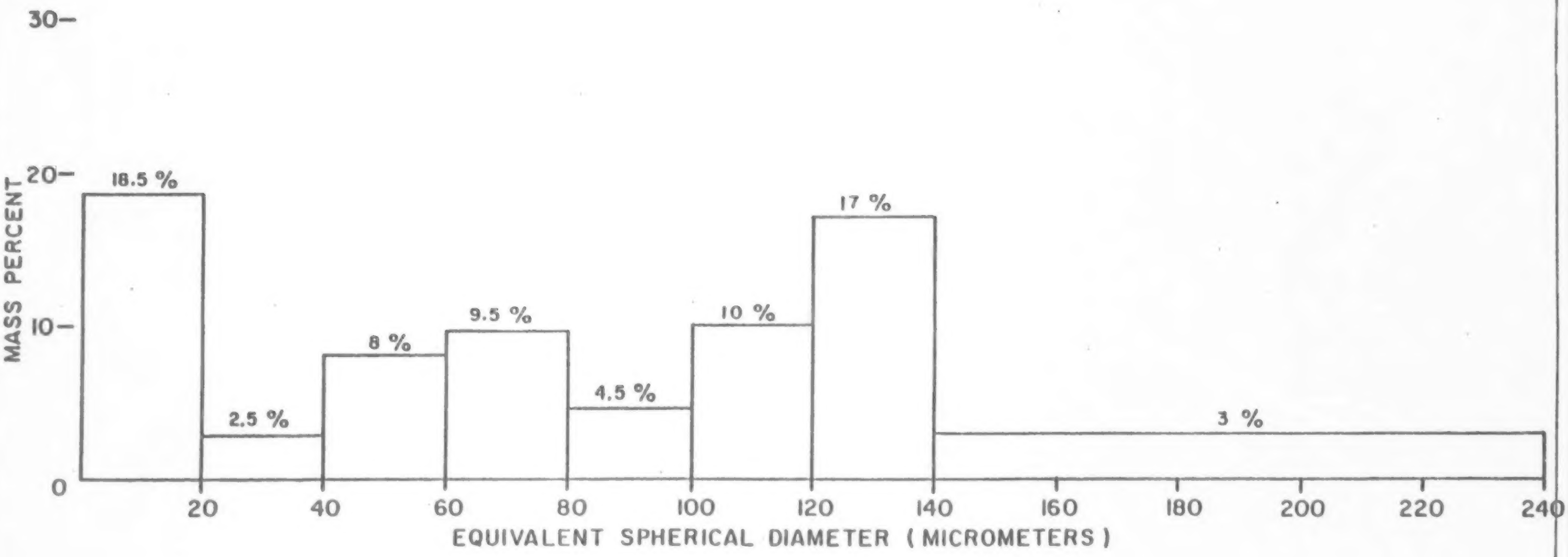
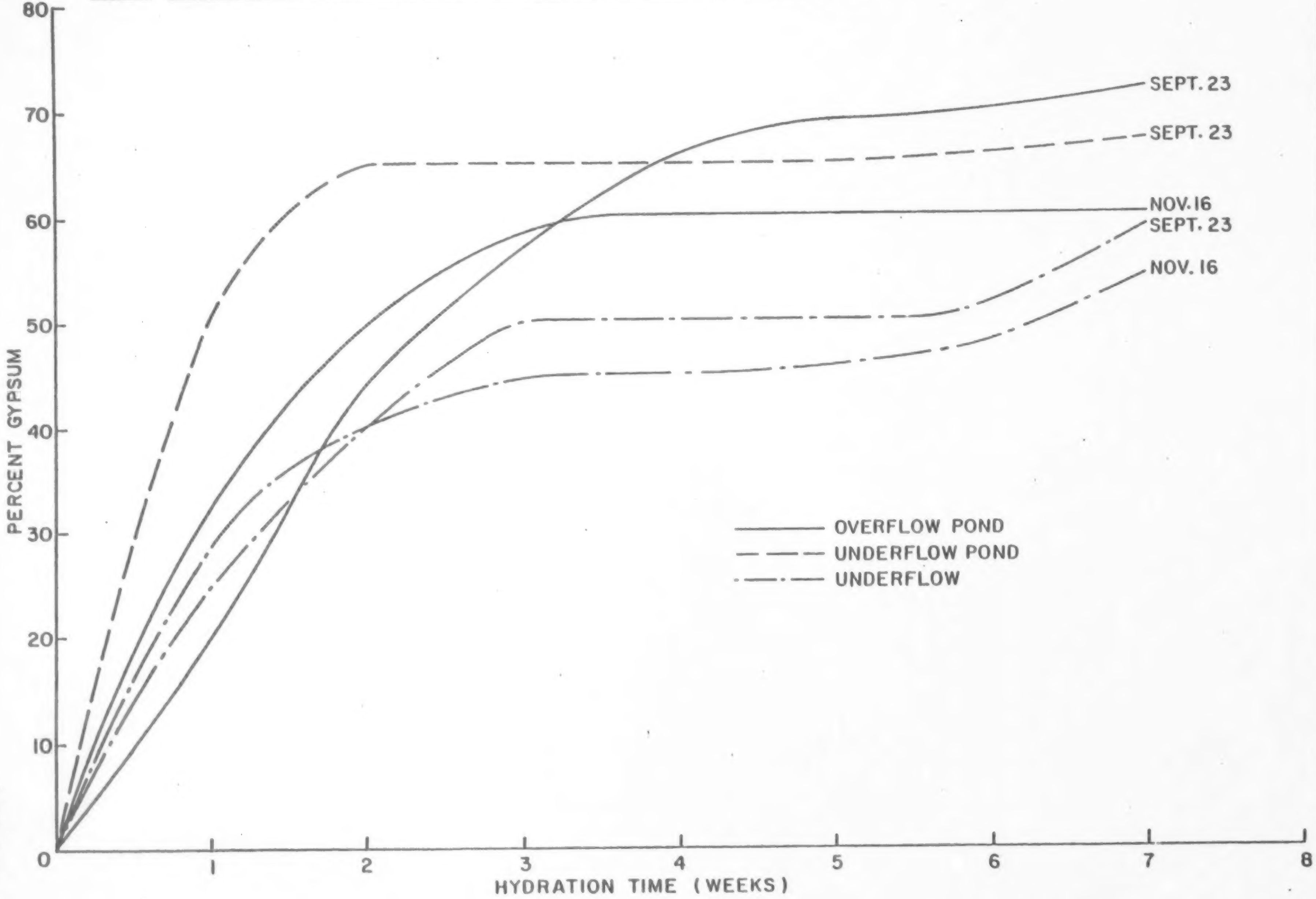


FIG.5 AVERAGE HYDRATION RATE OF HYDROCYCLONE EFFLUENTS



ORF

FIG. 6 AVERAGE COMPRESSIVE STRENGTH DEVELOPMENT OF HYDROCYCLONE EFFLUENTS

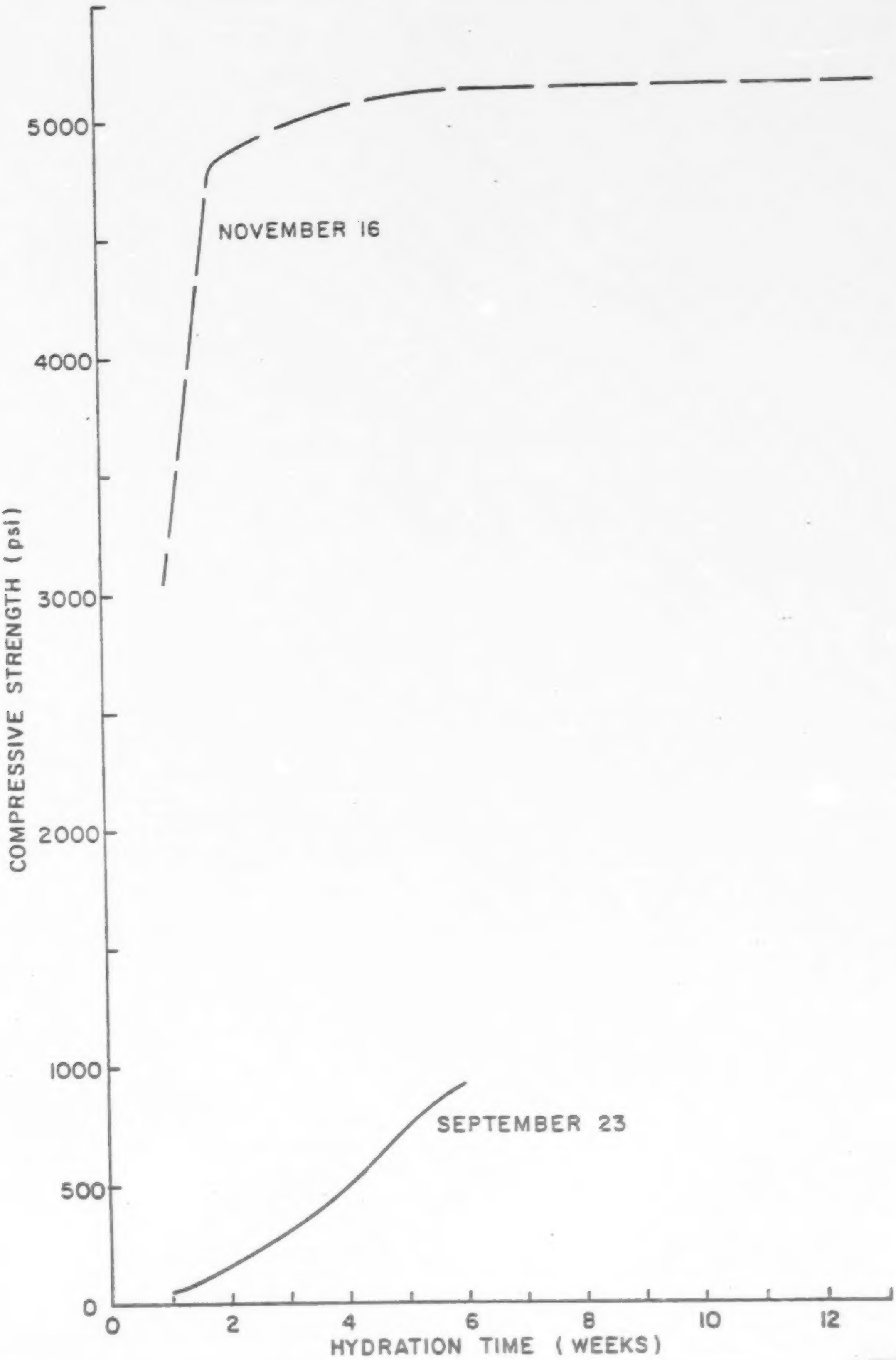
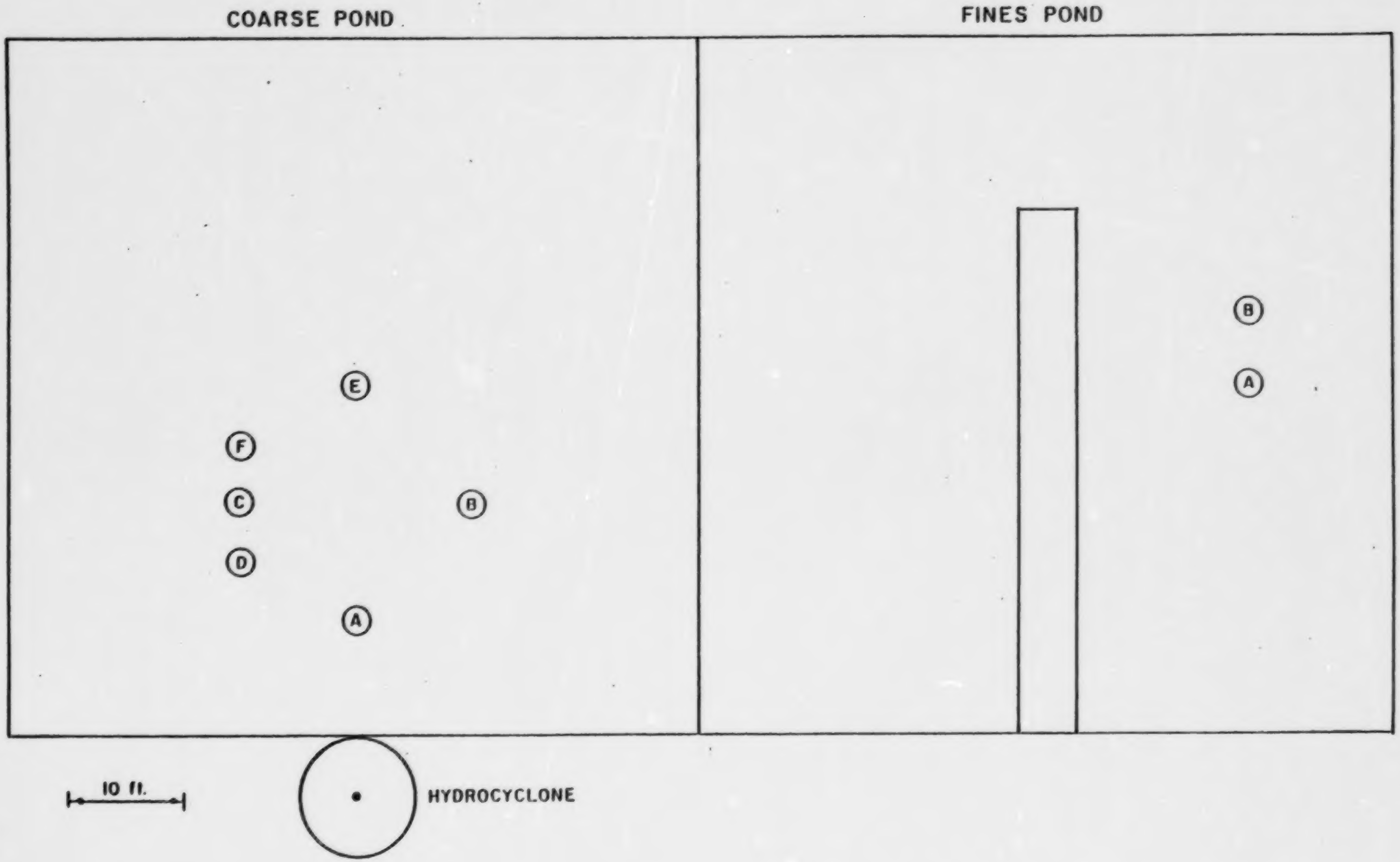


FIG.7 CORE SAMPLING LOCATIONS


COARSE POND
FINES POND
E
F
C
B
D
A
B
A
10 ft.
HYDROCYCLONE

ORF

FIG. 8 AVERAGE GYPSUM CONTENT OF CORE SAMPLES

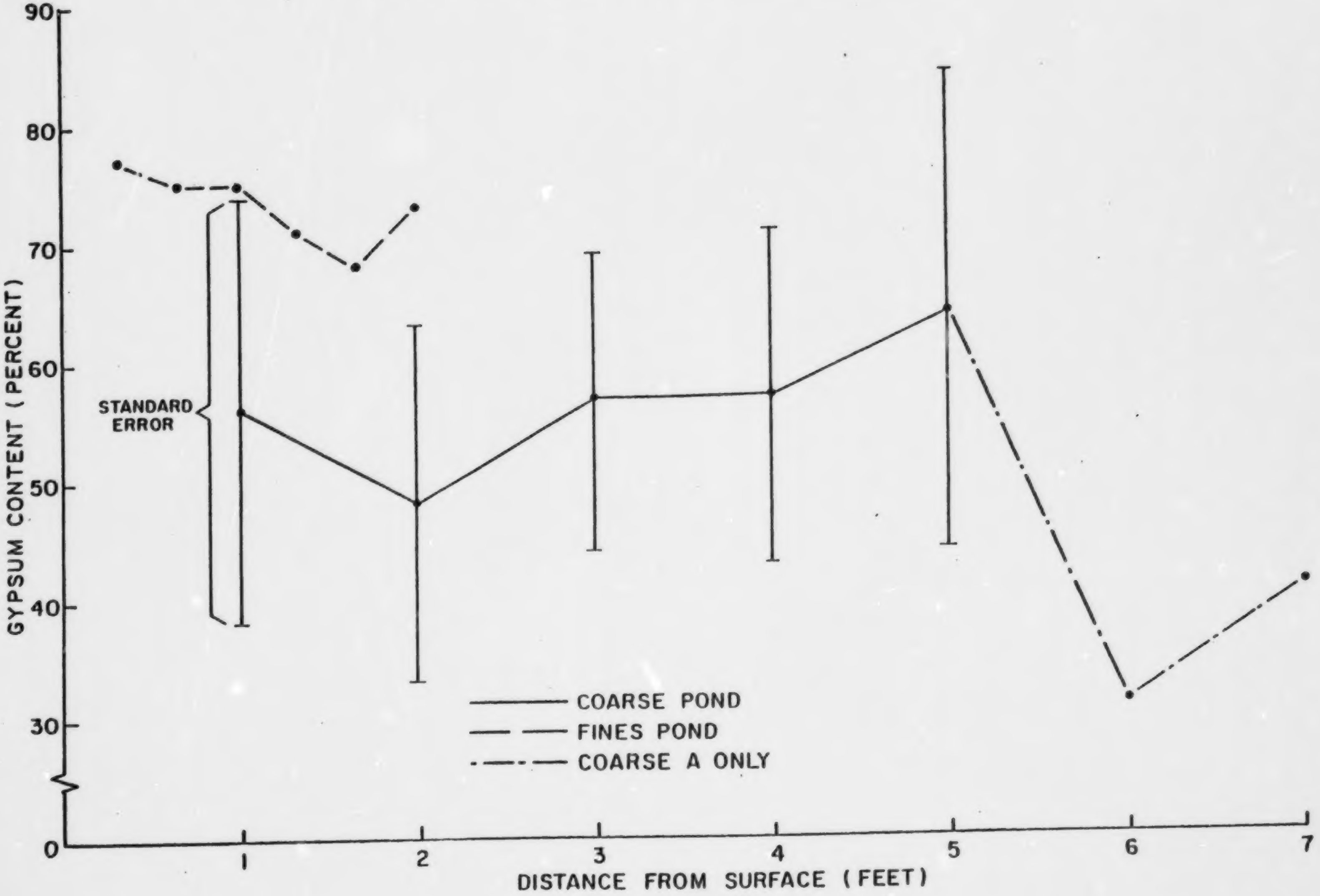
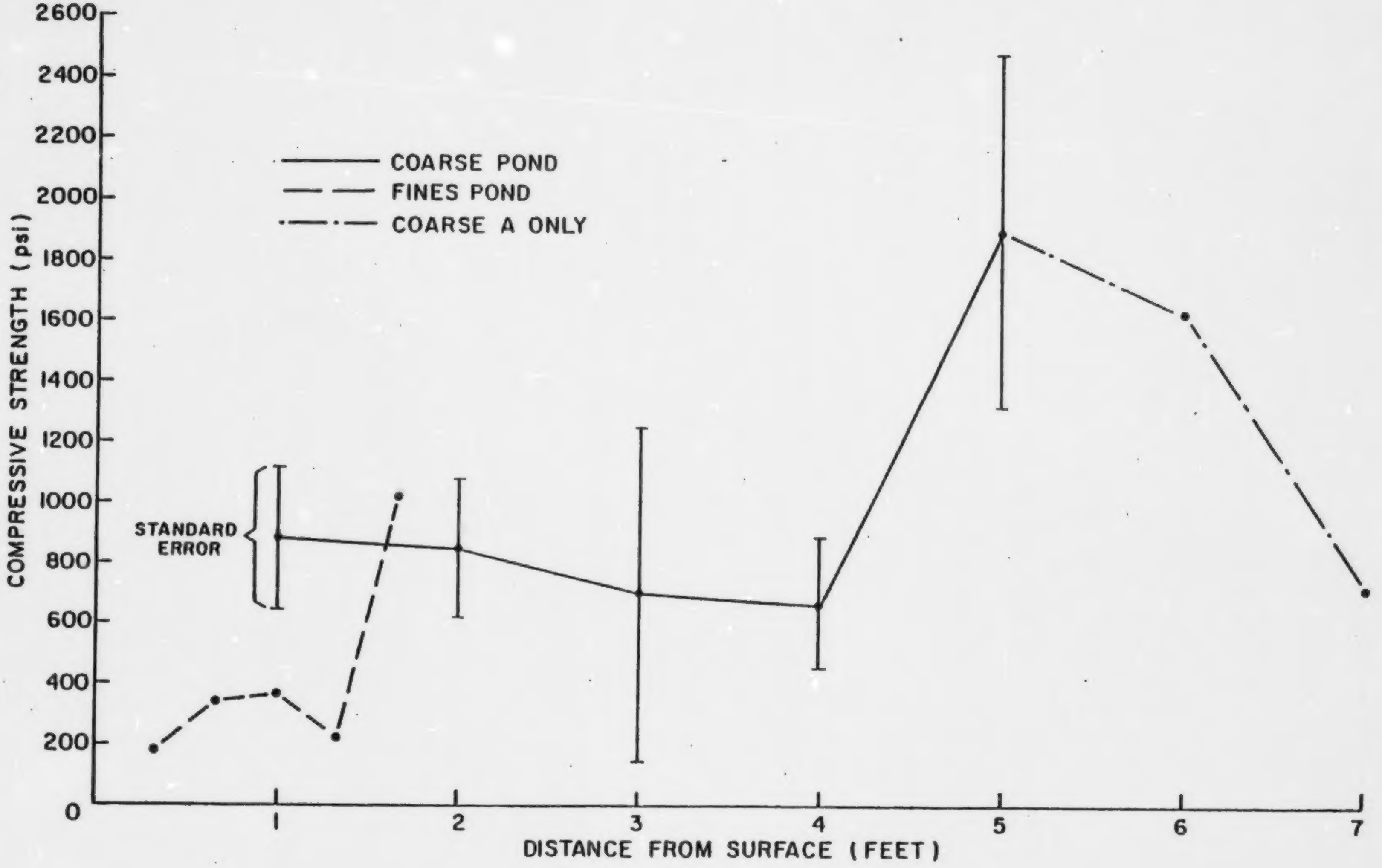


FIG. 9 AVERAGE COMPRESSIVE STRENGTH OF CORE SAMPLES



ATTACHMENT C

SYNOPSIS OF PROPOSED TEST PROGRAM - ST. LAWRENCE CEMENT CO.

The use of synthetic gypsum byproducts by cement manufacturers have been reported in various areas around the world. In 1978 and 1979, cement test grinds performed at St. Lawrence Cement, Mississauga plant, using the fluorogypsum byproduct of Allied Chemical indicated this material could be a viable gypsum source for use in cement production. However, due to impurities, handling problems developed especially during periods of freeze-thaw conditions. From studies performed at the Ontario Research Foundation, a method of removing a major portion of these impurities has been developed. Freeze-thaw studies performed on the purer product have shown that these problems should now be eliminated. To further assess the viability of the fluorogypsum, approximately 1,000 tonnes will be received at St. Lawrence in the fall 1982, for testing purposes.

The test program at St. Lawrence will be carried out in two phases. In the initial phase, Type 10 cement will be produced using the fluorogypsum. At the same time, Type 10 will also be produced using the natural gypsum rock. Separately, both cements will be tested for chemical and physical characteristics as specified under the A5 Portland Cement standard of the Canadian Standards Association. In addition to the above, separate laboratory concrete mixes will also be prepared from the cements.

The results of the above testing will serve two purposes. First, this will indicate that the cement produced with the fluorogypsum will meet the required specifications. Second, by comparing the cements, any chemical and physical differences that may result will be indicated. Based on the findings of these tests, other cement type test grinds using the fluorogypsum may also be carried out.

.../

At St. Lawrence Cement, gypsum rock is stockpiled outdoors on the property. For the second phase, a portion of the fluorogypsum will be stored outside through the winter and then used in test grinds similar to those performed in the fall. The results of these tests may provide more information on the effect of weathering to the physical characteristics and quality of the fluorogypsum.

Results for the first phase of testing should be available by January, 1983 while the final phase results should not be expected until the second quarter of 1983.

L. Zimmerman

LZ:HC

ST. LAWRENCE CEMENT, INC., MISSISSAUGA, TEST PROGRAM WITH ALLIED CHEMICAL GYPSUM BYPRODUCT

SUMMARY

At Allied Chemical, Amherstburg, Ontario, hydrogen fluoride is produced by combining calcium fluoride with sulphuric acid. This process results in a calcium sulphate byproduct being generated. In 1978 and 1979, investigations began at St. Lawrence Cement, Mississauga, to study the viability of using this waste byproduct as a source of gypsum in the manufacture of Portland cement. Positive indications for the use of this material were observed in the initial work but inherent impurities made handling impossible. Through research studies performed at the Ontario Research Foundation, a method was developed to remove a major portion of the impurities.

Beginning in October, 1982, a two-phase test program using the modified gypsum byproduct was carried out. The second phase of the program was completed by September, 1983. Results of the program have shown that the cement produced with the Allied Chemical gypsum met all the required specifications. No abnormal variations in the chemical and physical characteristics of the finished cement were observed while using this gypsum. In addition, no unusual handling

SUMMARY (CONT'D.)

problems with the gypsum byproduct were encountered throughout the test program.

INTRODUCTION

In general, to produce Portland cement, clinker with approximately 5% gypsum are interground in normally a ball mill to a desired fineness. The gypsum is added to regulate the setting time and early strength development of the cement paste. To a lesser extent, the gypsum also controls the shrinkage of the cement paste during curing. To produce the clinker, a chemically controlled ground mixture of limestone with lesser amounts of other additives such as shale or silica sand and iron are burnt in a kiln to a temperature of 1450°C.

At St. Lawrence Cement, Inc., Mississauga, three kilns are available for clinker production. One is a 4500 tonne per day dual four stage preheater-precalciner dry process kiln. The other two are identical 900 tonne per day wet process kilns. Utilizing the three kilns and the associated cement grinding mills, the plant has a rated production capacity of 2 million tonnes of Portland cement per year. At the rated capacity approximately 120 000 tonnes of gypsum would be required per annum.

One aspect for any industry, whether large or small, to be successful is that they are efficient in both operations and costs. Due to the aforementioned and also to environmental concerns, the use of byproducts that were at one time considered waste are now being utilized for various end uses.

INTRODUCTION (CONT'D.)

With this in mind, St. Lawrence Cement, Mississauga and Allied Chemical began investigating the possibility of using the gypsum byproduct of Allied Chemical as an additive for Portland cement manufacture.

In 1978 and 1979, Portland cement test grinds using the gypsum byproduct were performed at Mississauga. The initial indications were that this material could be a viable gypsum source for use in Portland cement manufacture. However, due to impurities, handling problems developed especially during periods of freeze-thaw conditions. From studies performed at the Ontario Research Foundation, a method was developed to remove the major portion of these impurities.

To assess the viability of using the modified Allied Chemical gypsum byproduct, 1230 tonnes of the material was received at St. Lawrence Cement, Mississauga, in October, 1982, for testing purposes.

The test program that was carried out would serve three purposes. First it was important to determine if the cement produced with the gypsum byproduct would meet the required specifications. Second, to investigate if unusual variations to the chemical and physical characteristics of the finished cement would result through the use of this gypsum byproduct. Third, to examine if short and longer term stockpiling would effect the chemical and physical characteristics of the gypsum byproduct.

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TEST PROGRAM

The test program at Mississauga was carried out in two phases. On December 15, 1982, the first phase of the program began with a 24 hour production test grind of Type 10 cement using the Allied Chemical gypsum. Simultaneously on an identical mill, Type 10 cement was produced using natural gypsum. During the grinding, Blaine fineness checks and %SO_3 determinations using X-Ray Fluorescence were performed every hour on each mill. A portion of the hourly samples were retained. Upon completion of the grinding, separate cement composite samples were prepared by blending the individual hourly samples. Each composite was then tested according to Canadian Standards Association (CSA) and American Society for Testing Materials (ASTM) specifications. In addition, laboratory concrete mixes were prepared from each of the cement composites.

For the second phase of the test program, the remaining Allied Chemical gypsum was stockpiled outside on the plant property and then on July 19, 1983 was again used in a 24 hour production test grind of Type 10 cement. Similar to the first phase, a simultaneous grind using natural gypsum was also carried out. The controlling and testing were identical to that of the first phase. Samples of the gypsum feeding each mill were taken during the grinding and also were tested.

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TEST RESULTS AND DISCUSSIONS

The results for Phase #1 of the program, are shown in Tables 1, 2 and 3. Chemically, the differences between the Type 10 cement ground with Allied Chemical gypsum and that produced with natural gypsum were minimal. The variations that did exist were those typically encountered under normal operation. One interesting comparison that could be made was with the "% insoluble residue" results. The considerably lower results obtained with the Allied Chemical gypsum indicates it is a purer form of gypsum. Similar to the chemical results, the comparison of physical results agreed very well for all parameters. The slight differences that did exist were those expected for normal operation. Keeping in line with the aforementioned comparisons, the concrete results agreed very well. The slightly higher penetration setting times observed in the concrete made from the cement produced with Allied Chemical gypsum are not considered significant as they are within the ASTM interlaboratory standard deviation for this test method. Although cannot be explained and by no means detrimental were the higher compressive strengths achieved in the concrete prepared from the cement which was ground with the Allied Chemical gypsum.

The Type 10 cement comparisons for Phase #2 of the test program are shown in Tables 4, 5 and 6. Generally, the comparisons were very similar to those observed in Phase #1. Chemically, only slight variations existed and again could be attributed to those expected under typical operation.

TEST RESULTS AND DISCUSSIONS (CONT'D.)

In comparing the physical results, increases in the air content and setting time were observed in the cement produced with the Allied Chemical gypsum. All other parameters agreed very well. Because of the higher air content in the mortar testing, air content comparisons were also performed in the concrete testing. As shown, there was no significant increases when comparing the concrete mixes. In addition the longer mortar setting time observed with the Type 10 cement produced with the Allied Chemical gypsum had no effect when the same cement was used in concrete.

No apparent effects were encountered in the Allied Chemical gypsum due to weathering. The gypsum maintained its coarse rock appearance in the stockpile after outside winter storage. Prior to use in the July 1983 grind, no unusual difficulties in handling and crushing were encountered. The comparison analysis for the Allied Chemical and natural gypsums are shown in Table #7. The Allied Chemical gypsum was higher in total %$CaSO_4$ than the natural gypsum and as indicated also contains a greater quantity of anhydrite gypsum. This is particularly beneficial for counteracting false set (early stiffening) characteristics of cement which occassionally occurs due to excessive milling temperatures. The purity of the Allied Chemical gypsum first mentioned in the Phase #1 results are again shown by the lower % insoluble results.

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CONCLUSIONS

Based on the results of this test program, the viability of using the Allied Chemical gypsum for Portland cement manufacture has been shown. At no time during the testing were detrimental effects encountered in the finished cement through the use of this material. The handling problems that were observed in the 1978 and 1979 testing of the gypsum byproduct were not encountered during this test program.

L. Zimmerman
Chief Chemist

CHEMICAL RESULTS

TEST #1

1982 12 15

TYPE 10 CEMENT

% COMPOSITION	ALLIED CHEMICAL GYPSUM	NATURAL GYPSUM
LOI	.71	.99
SiO_2	20.61	20.52
Al_2O_3	6.32	6.29
Fe_2O_3	2.03	2.07
CaO	63.53	63.14
MgO	2.78	2.78
SO_3	2.48	2.62
K_2O	1.19	1.21
Na_2O	.23	.24
Cl	.07	.06
Insoluble	.10	.23
C_3S	49.5	47.8
C_2S	21.8	22.8
C_3A	13.3	13.2
C_4AF	6.2	6.3

LOI - Loss on Ignition
C_3S - Tricalcium Silicate
C_2S - Dicalcium Silicate
C_3A - Tricalcium Aluminate
C_4AF - Tetracalcium Aluminoferrite

TABLE 1

PHYSICAL RESULTS

TEST #1

1982 12 15

TYPE 10 CEMENT

	Allied Chemical Gypsum	Natural Gypsum
Blaine m^2/kg	324	331
Residue % 75µm	1.6	3.0
Vicat Set min.	140	135
False Set %	96.4	88.2
Air Content %	9.0	9.5
Autoclave Expansion %	.13	.13
Compressive Strength MPa		
1 Day	13.1	12.7
3 Day	21.1	21.2
7 Day	25.7	23.7
28 Day	31.8	29.2

TABLE 2

CONCRETE RESULTS

TEST #1

1982 12 15

TYPE 10 CEMENT

	ALLIED CHEMICAL GYPSUM	NATURAL GYPSUM
Mix Design kg/m^3		
Cement	255	255
Coarse Aggregate	1068	1068
Fine Aggregate	884	884
Water	162	163
Slump mm	85	85
Compressive Strength MPa		
1 Day	10.4	10.4
2 Day	24.0	22.2
7 Day	28.7	27.0
28 Day	35.3	32.6
Setting Time (Penetration Resistance) MPa		
4 hr	0.2	0.6
5 hr	1.8	2.6
6 hr	4.3	8.3
7 hr	7.7	15.2
7.5 hr	32.5	36.4
Initial Set 3.5 MPa	5.9 hr	5.4 hr
Final Set 27.6 MPa	7.6 hr	7.3 hr

TABLE 3

CHEMICAL RESULTS

TEST #2

1983 07 19

TYPE 10 CEMENT

% COMPOSITION	ALLIED CHEMICAL GYPSUM	NATURAL GYPSUM
LOI	.61	.69
SiO_2	20.36	20.54
Al_2O_3	6.12	6.41
Fe_2O_3	2.07	2.04
CaO	63.69	63.83
MgO	2.60	2.71
SO_3	2.92	2.98
K_2O	1.29	1.28
Na_2O	.24	.24
Cl	.08	.08
Insoluble	.13	.22
C_3S	52.1	49.2
C_2S	19.2	21.8
C_3A	12.7	13.5
C_4AF	6.3	6.2

LOI - Loss on Ignition
C_3S - Tricalcium Silicate
C_2S - Dicalcium Silicate
C_3A - Tricalcium Aluminate
C_4AF - Tetracalcium Aluminoferrite

TABLE 4

PHYSICAL RESULTS

TEST #2

1983 07 19

TYPE 10 CEMENT

	ALLIED CHEMICAL GYPSUM	NATURAL GYPSUM
Blaine m^2/kg	363	361
Residue % 75µm	.5	1.4
Vicat Set min.	133	112
False Set %	100.0	85.7
Air Content %	11.0	9.6
Autoclave Expansion %	.16	.17
Compressive Strength - MPa		
1 Day	15.8	17.2
3 Day	24.4	26.1
7 Day	29.0	29.3
28 Day	34.6	35.0

TABLE 5

CONCRETE RESULTS

TEST #2

1983 07 19

TYPE 10 CEMENT

	ALLIED CHEMICAL GYPSUM	NATURAL GYPSUM
Mix Design kg/m³		
Cement	255	255
Coarse Aggregate	1068	1068
Fine Aggregate	884	884
Water	164	167
Slump mm	85	85
Air Content %	2.4	2.3
Compressive Strength MPa		
1 Day	17.6	17.1
3 Day	25.5	25.6
7 Day	29.6	29.2
28 Day	34.5	34.0
Setting Time (Penetration Resistance) MPa		
3 hr	.8	1.1
4 hr	5.5	7.7
5 hr	23.2	25.4
5.5 hr	41.9	42.7
Initial Set - 3.5 MPa	3.8 hr	3.6 hr
Final Set - 27.6 MPa	5.1 hr	5.1 hr

TABLE 6

ST. LAWRENCE CEMENT, INC., MISSISSAUGA, TEST PROGRAM WITH ALLIED CHEMICAL GYPSUM BYPRODUCT

SUMMARY

At Allied Chemical, Amherstburg, Ontario, hydrogen fluoride is produced by combining calcium fluoride with sulphuric acid. This process results in a calcium sulphate byproduct being generated. In 1978 and 1979, investigations began at St. Lawrence Cement, Mississauga, to study the viability of using this waste byproduct as a source of gypsum in the manufacture of Portland cement. Positive indications for the use of this material were observed in the initial work but inherent impurities made handling impossible. Through research studies performed at the Ontario Research Foundation, a method was developed to remove a major portion of the impurities.

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SUMMARY (CONT'D.)

problems with the gypsum byproduct were encountered throughout the test program.

INTRODUCTION

In general, to produce Portland cement, clinker with approximately 5% gypsum are interground in normally a ball mill to a desired fineness. The gypsum is added to regulate the setting time and early strength development of the cement paste. To a lesser extent, the gypsum also controls the shrinkage of the cement paste during curing. To produce the clinker, a chemically controlled ground mixture of limestone with lesser amounts of other additives such as shale or silica sand and iron are burnt in a kiln to a temperature of 1450°C.

At St. Lawrence Cement, Inc., Mississauga, three kilns are available for clinker production. One is a 4500 tonne per day dual four stage preheater-precalciner dry process kiln. The other two are identical 900 tonne per day wet process kilns. Utilizing the three kilns and the associated cement grinding mills, the plant has a rated production capacity of 2 million tonnes of Portland cement per year. At the rated capacity approximately 120 000 tonnes of gypsum would be required per annum.

One aspect for any industry, whether large or small, to be successful is that they are efficient in both operations and costs. Due to the aforementioned and also to environmental concerns, the use of byproducts that were at one time considered waste are now being utilized for various end uses.

INTRODUCTION (CONT'D.)

With this in mind, St. Lawrence Cement, Mississauga and Allied Chemical began investigating the possibility of using the gypsum byproduct of Allied Chemical as an additive for Portland cement manufacture.

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To assess the viability of using the modified Allied Chemical gypsum byproduct, 1230 tonnes of the material was received at St. Lawrence Cement, Mississauga, in October, 1982, for testing purposes.

The test program that was carried out would serve three purposes. First it was important to determine if the cement produced with the gypsum byproduct would meet the required specifications. Second, to investigate if unusual variations to the chemical and physical characteristics of the finished cement would result through the use of this gypsum byproduct. Third, to examine if short and longer term stockpiling would effect the chemical and physical characteristics of the gypsum byproduct.

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TEST PROGRAM

The test program at Mississauga was carried out in two phases. On December 15, 1982, the first phase of the program began with a 24 hour production test grind of Type 10 cement using the Allied Chemical gypsum. Simultaneously on an identical mill, Type 10 cement was produced using natural gypsum. During the grinding, Blaine fineness checks and %SO_3 determinations using X-Ray Fluorescence were performed every hour on each mill. A portion of the hourly samples were retained. Upon completion of the grinding, separate cement composite samples were prepared by blending the individual hourly samples. Each composite was then tested according to Canadian Standards Association (CSA) and American Society for Testing Materials (ASTM) specifications. In addition, laboratory concrete mixes were prepared from each of the cement composites.

For the second phase of the test program, the remaining Allied Chemical gypsum was stockpiled outside on the plant property and then on July 19, 1983 was again used in a 24 hour production test grind of Type 10 cement. Similar to the first phase, a simultaneous grind using natural gypsum was also carried out. The controlling and testing were identical to that of the first phase. Samples of the gypsum feeding each mill were taken during the grinding and also were tested.

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TEST RESULTS AND DISCUSSIONS

The results for Phase #1 of the program, are shown in Tables 1, 2 and 3. Chemically, the differences between the Type 10 cement ground with Allied Chemical gypsum and that produced with natural gypsum were minimal. The variations that did exist were those typically encountered under normal operation. One interesting comparison that could be made was with the "% insoluble residue" results. The considerably lower results obtained with the Allied Chemical gypsum indicates it is a purer form of gypsum. Similar to the chemical results, the comparison of physical results agreed very well for all parameters. The slight differences that did exist were those expected for normal operation. Keeping in line with the aforementioned comparisons, the concrete results agreed very well. The slightly higher penetration setting times observed in the concrete made from the cement produced with Allied Chemical gypsum are not considered significant as they are within the ASTM interlaboratory standard deviation for this test method. Although cannot be explained and by no means detrimental were the higher compressive strengths achieved in the concrete prepared from the cement which was ground with the Allied Chemical gypsum.

The Type 10 cement comparisons for Phase #2 of the test program are shown in Tables 4, 5 and 6. Generally, the comparisons were very similar to those observed in Phase #1. Chemically, only slight variations existed and again could be attributed to those expected under typical operation.

TEST RESULTS AND DISCUSSIONS (CONT'D.)

In comparing the physical results, increases in the air content and setting time were observed in the cement produced with the Allied Chemical gypsum. All other parameters agreed very well. Because of the higher air content in the mortar testing, air content comparisons were also performed in the concrete testing. As shown, there was no significant increases when comparing the concrete mixes. In addition the longer mortar setting time observed with the Type 10 cement produced with the Allied Chemical gypsum had no effect when the same cement was used in concrete.

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CONCLUSIONS

Based on the results of this test program, the viability of using the Allied Chemical gypsum for Portland cement manufacture has been shown. At no time during the testing were detrimental effects encountered in the finished cement through the use of this material. The handling problems that were observed in the 1978 and 1979 testing of the gypsum byproduct were not encountered during this test program.

L. Zimmerman
Chief Chemist

CHEMICAL RESULTS

TEST #1

1982 12 15

TYPE 10 CEMENT

% COMPOSITION	ALLIED CHEMICAL GYPSUM	NATURAL GYPSUM
LOI	.71	.99
SiO_2	20.61	20.52
Al_2O_3	6.32	6.29
Fe_2O_3	2.03	2.07
CaO	63.53	63.14
MgO	2.78	2.78
SO_3	2.48	2.62
K_2O	1.19	1.21
Na_2O	.23	.24
Cl	.07	.06
Insoluble	.10	.23
C_3S	49.5	47.8
C_2S	21.8	22.8
C_3A	13.3	13.2
C_4AF	6.2	6.3

LOI - Loss on Ignition
C_3S - Tricalcium Silicate
C_2S - Dicalcium Silicate
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C_4AF - Tetracalcium Aluminoferrite

TABLE 1

PHYSICAL RESULTS

TEST #1

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TYPE 10 CEMENT

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False Set %	96.4	88.2
Air Content %	9.0	9.5
Autoclave Expansion %	.13	.13
Compressive Strength MPa		
1 Day	13.1	12.7
3 Day	21.1	21.2
7 Day	25.7	23.7
28 Day	31.8	29.2

TABLE 2

CONCRETE RESULTS

TEST #1

1982 12 15

TYPE 10 CEMENT

	ALLIED CHEMICAL GYPSUM	NATURAL GYPSUM
Mix Design kg/m³		
Cement	255	255
Coarse Aggregate	1068	1068
Fine Aggregate	884	884
Water	162	163
Slump mm	85	85
Compressive Strength MPa		
1 Day	10.4	10.4
2 Day	24.0	22.2
7 Day	28.7	27.0
28 Day	35.3	32.6
Setting Time (Penetration Resistance) MPa		
4 hr	0.2	0.6
5 hr	1.8	2.6
6 hr	4.3	8.3
7 hr	7.7	15.2
7.5 hr	32.5	36.4
Initial Set 3.5 MPa	5.9 hr	5.4 hr
Final Set 27.6 MPa	7.6 hr	7.3 hr

TABLE 3

CHEMICAL RESULTS

TEST #2

1983 07 19

TYPE 10 CEMENT

% COMPOSITION	ALLIED CHEMICAL GYPSUM	NATURAL GYPSUM
LOI	.61	.69
SiO_2	20.36	20.54
Al_2O_3	6.12	6.41
Fe_2O_3	2.07	2.04
CaO	63.69	63.83
MgO	2.60	2.71
SO_3	2.92	2.98
K_2O	1.29	1.28
Na_2O	.24	.24
Cl	.08	.08
Insoluble	.13	.22
C_3S	52.1	49.2
C_2S	19.2	21.8
C_3A	12.7	13.5
C_4AF	6.3	6.2

LOI - Loss on Ignition
C_3S - Tricalcium Silicate
C_2S - Dicalcium Silicate
C_3A - Tricalcium Aluminate
C_4AF - Tetracalcium Aluminoferrite

TABLE 4

PHYSICAL RESULTS

TEST #2

1983 07 19

TYPE 10 CEMENT

	ALLIED CHEMICAL GYPSUM	NATURAL GYPSUM
Blaine m²/kg	363	361
Residue % 75µm	.5	1.4
Vicat Set min.	133	112
False Set %	100.0	85.7
Air Content %	11.0	9.6
Autoclave Expansion %	.16	.17
Compressive Strength - MPa		
1 Day	15.8	17.2
3 Day	24.4	26.1
7 Day	29.0	29.3
28 Day	34.6	35.0

TABLE 5

CONCRETE RESULTS

TEST #2

1983 07 19

TYPE 10 CEMENT

	ALLIED CHEMICAL GYPSUM	NATURAL GYPSUM
Mix Design kg/m³		
Cement	255	255
Coarse Aggregate	1068	1068
Fine Aggregate	884	884
Water	164	167
Slump mm	85	85
Air Content %	2.4	2.3
Compressive Strength MPa		
1 Day	17.6	17.1
3 Day	25.5	25.6
7 Day	29.6	29.2
28 Day	34.5	34.0
Setting Time (Penetration Resistance) MPa		
3 hr	.8	1.1
4 hr	5.5	7.7
5 hr	23.2	25.4
5.5 hr	41.9	42.7
Initial Set - 3.5 MPa	3.8 hr	3.6 hr
Final Set - 27.6 MPa	5.1 hr	5.1 hr

TABLE 6

ATTACHMENT D

CIL EXPLOSIVES DIVISION, "REPORT ON
CRATER TESTS AND BLAST RECOMMENDATIONS"

C·I·L Inc.

C·I·L House
P.O. Box 200, Station "A"
Willowdale, Ontario M2N 6H2
(416) 229-7000 Telex 06986505

October 6, 1982.

cc: Mr. R. Shaw - Allied Chemical
Mr. C. McNeil - Allied Chemical

Mr. R. Searcy
Allied Chemical Co.
P.O. Box 2000
Amherstburg, Ontario
N9V 2Z6

Dear Mr. Searcy,

Stephen Chung and I have completed our work on a blast design for recovery of gypsum from the old Allied Chemical quarry and a copy of our report is enclosed. Also included is a copy of the high speed film taken of the test blasts. The film shows the three blasts shot September 9, 1982.

We appreciate the organization and cooperation shown by Allied personnel during the test blasts.

If it is possible, we would like any information your vibration consultant, VME, may have on the vibration level caused by different charges within each blast. This would be used for our ongoing research into blast phenomena.

Best wishes on the successful completion of your project.

Yours truly,

Paul Tidman

Paul Tidman
Blasting Physicist

PT/el
Encl.

C-I-L Inc.
Explosives Division
Consulting Services Group

REPORT ON CRATER TESTS AND BLAST RECOMMENDATIONS AT ALLIED CHEMICAL CO., AMHERSTBURG, ONTARIO

Prepared by:
S. Chung &
J.P. Tidman
Willowdale, Ontario
October 6, 1982.

SUMMARY

The results of crater tests recommend the blasting of gypsum using short (6 diameter) charges with a powder factor of .3 kg/m³ for AMEX or HYDROGEL in 150 mm diameter holes.

Crater Tests

A set of test blasts were loaded and shot to establish the basis for a blast design. Excluding the first test blast, holes were loaded with a fixed charge weight while the depth of the charge varied from hole to hole. The charge which produces the optimum blast in the test series then forms the reference for scaling the blast to larger charges.

As outlined in S. Chung's letter to R.L. Searcy (see Appendix), the holes were 100mm diameter, drilled to various depths and regularly spaced. Unfortunately, on the day of the tests, September 9, 1982, the water table was high and many of the holes were wet. The vacuum tank truck could not dewater these holes, so they were backfilled to the water table. This allowed the use of AMEX II, a dry blasting agent with no water resistance, as the test explosive.

The holes were loaded with 4.7 litres of AMEX II (3.95 kg) and primed with a cast booster (.45 kg). The charge length was thus limited to 6 borehole diameters, a practical limit for scaling explosion effects. The two main test blasts each consisted of 10 holes, fired on even short period delays from # 0 to # 18. The spacing of the boreholes and the time delays ensured that each charge acted independently.

Following the blasts, the characteristics of each blasthole were recorded and the resulting crater excavated by a hydraulic backhoe. The resulting crater volumes were used to evaluate the success of each particular charge. Details of the charge position and resulting craters are given in Table 1. Figures 1, 2 and 3 contain photographs of the craters and muck for some of the larger craters.

A feature of crater tests is the graph of crater volume vs. charge depth. The results can be represented by a curve which rises as charge burial increases. The curve reaches a maximum at a depth termed the optimum charge depth. The curve then falls to zero at what is called the critical depth.

Because the charge length was limited to 6 borehole diamters, we can use the property that distances associated with equivalent blast effects scale with the cube root of the charge weight. The scaled dimensions of the test craters are shown in Figure 4. The scaled crater volume has a sharp maximum around a charge depth of .7 $m/kg^{1/3}$ before dropping to zero around .8 $m/kg^{1/3}$. The sharp peak is typical of crater tests in plastic material such as permafrost.

During the test blasts, maximum flyrock range was 50 m and vibration intensities did not exceed 40 mm/s peak particle velocity at distances from the charge greater than 20m. Fragmentation from craters at optimum depth was considered good and the resulting muck was dug easily.

Blast Design

The test blasts showed that effective blasting could be achieved with relatively low specific explosives consumption. The selected borehole diameter controls the ultimate blast design as the charge weight is proportional to $diameter^3$. At the test blast site, it was noted that holes drilled well into the water table had filled in. Long boreholes may then be lost as the water table rises or in very wet weather. To avoid this 6 inch diameter auger holes are proposed. This diameter also results in convenient charge weights for packaged slurry explosives.

An AMEX charge 6 diameters long weighs 14.5 kg. for the selected hole diameter. Using this charge weight and the scaled crater dimensions at optimum charge, a pattern of holes spaced 4.25 m (14 ft.) drilled to a depth of 2.1 m (7 ft) is determined. As with the test blasts, breakage below the bottom of the hole can be expected, perhaps to a depth of 2.5 m (8 ft).

Since the crater test results are specific to AMEX and the gypsum material, computer calculations must be used to find water-resistant slurry loads which can produce the same blast results. A program writtem specifically to analyze crater blasts, termed VCR, was used to find the optimum depth for several slurry explosive loads (see Table 2). The charges giving optimum depths close to the AMEX value of 1.8 m were then used in a comparison of blast performance on C-I-L's BOBCAT program. While the performance is in terms of bench blasting (see figure 5), the excellent results for blasting using the the three blast designs ensures equivalent performance(Table 3). The rock properties needed for the computer blasting programs were measured and are given in Table 4.

Blast Hookup

The explosives selected for the blasting pattern are cap-insensitive products which require a cast booster for initiation. Standard priming practice is to use a Procore booster with a detonating cord downline. This would lead to significant noise from the initiation system. Short period electric detonators (5m) in the Booster will give a silent initiation system. A non-electric alternative is to use NONEL detonators (5m) in the booster and NONEL No-Noise connectors on surface.

Holes should be delayed with short period detonators so that central holes in the pattern fire first, with subsequent delays advancing towards to corners (see figure 6). The number of holes per delay will depend on the vibration constraints but it is not necessary, even for the first firing period, to shoot one hole per delay. Charges should be well-stemmed.

Recommendations

The gypsum at Allied Chemical can be blasted with AMEX or HYDROGEL using the following pattern:

Burden = 4.25 m
Spacing = 4.25
Hole diameter = 150mm
Hole depth = 2.1m
Charge = 14.5 kg AMEX or HYDROGEL (125mm)

The resulting blast will produce a layer of material broken to a depth of 2.5m; permitting excavation by a front-end loader. The effective powder factor will then be .3kg/m³.

Table 1a

Allied Chemical Crater Tests

Charge Weight = 4.4 kg AMEX II + PROCORE

Blast # 2

Period	Charge Location			Crater Dimensions				
	Length(m)	Depth(m)	Scaled Depth (m/kg 1/3)	Diameter (m) Top	Diameter (m) Bottom	Depth (m)	Volume (m^3)	Scaled Volume (m^3/kg)
0	.18	2.13	1.3	-	-	-	-	intact
2	.66	1.35	.82	-	-	-	-	intact
4	.43	.99	.60	2.59	.91	.91	2.36	.54
6	.56	1.88	1.15	-	-	-	-	intact
8	.48	1.47	.90	-	-	-	-	intact
10	.53	1.22	.74	-	-	-	-	uplift
12	.61	.61	.37	1.5	1.1	.69	.92	.21
14	.61	1.35	.82	3.35	1.5	1.3	6.1	1.38
16	.53	.97	.59	3.96	1.5	2.0	12.6	2.85
18	.38	1.22	.74	4.5	2.0	2.0	17.4	3.96

Table 1b

Allied Chemical Crater Tests

Charge Weight = 4.4 kg AMEX II + PROCORE

Blast # 3

Period	Charge Location			Crater Dimentions				
	Length(m)	Depth(m)	Scaled Depth (m/kg 1/3)	Diameter (m) Top	Diameter (m) Bottom	Depth (m)	Volume (m^3)	Scaled Volume (m^3/kg)
0	.56	1.32	.81					intact
2	.58	1.42	.87					intact
4	.61	1.52	.93					intact
6	.53	1.27	.78					uplift
8	.61	1.22	.74					intact
10	.56	1.55	.95					intact
12	.56	1.02	.62	4.0	1.2	1.1	6.2	1.4
14	.53	1.27	.76	4.6	1.8	1.7	14.3	3.26
16	.58	1.04	.64	3.8	1.5	1.7	9.9	2.26
18	.53	.97	.59	3.5	1.5	1.5	7.9	1.79

Table 2

VCR Analysis of Allied Chemical Craters

Explosive	Density (g/cm³) Package	 Borehole	Charge Length (m)	Charge Weight (kg)	Optimum Depth(m)	Borehole Depth(m)
AMEX	-	.84	.91	14.5	1.81	2.27
Nitropel*	-	1.05	.91	17.3	2.31	2.76
Hydrogel+ (125mm)	1.25	.87	.91	14.5	1.81	2.27
Hydromex T-3+ (125mm)	1.45	1.01	.70	12.5	2.03	2.38

+ packaged slurry explosive with excellent water resistance

* free-running explosive with excellent water resistance

Table 3

BOBCAT Analysis of Allied Chemical Blast Designs

6" Diameter holes

Burden = Spacing = 4.25m (14 ft)

Hole Depth = 2.1m (7 ft)

Explosive	Weight (kg)	Performance				
		Grade	Column	Collar	Heave	Flyrock
ANFO+	14.5	100	100	100	100	100
Hydrogel	14.5	100	100	99	99	100
Hydromex T-3	12.5	101	92	97	82	88

+ As reference blast, performance is assigned a value of 100.

Table 4

Rock Properties of Allied Chemical Gypsum

Density (g/cm^3)	2.1
Young's Modulus (kbar)	190
Poisson's Ratio	.01
P-wave velocity (km/s)	3.0
S-wave velocity (km/s)	2.1

Figure 1

Photos of Crater Period 18

from Blast #2 at Allied Chemical

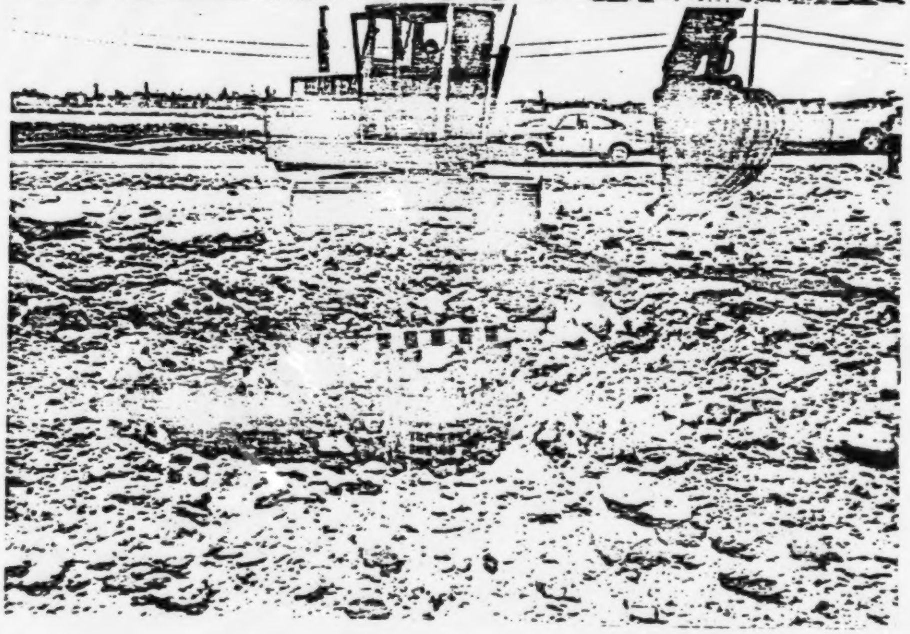


Figure 2

Photos of Crater Period 14

from Blast #2 at Allied Chemical

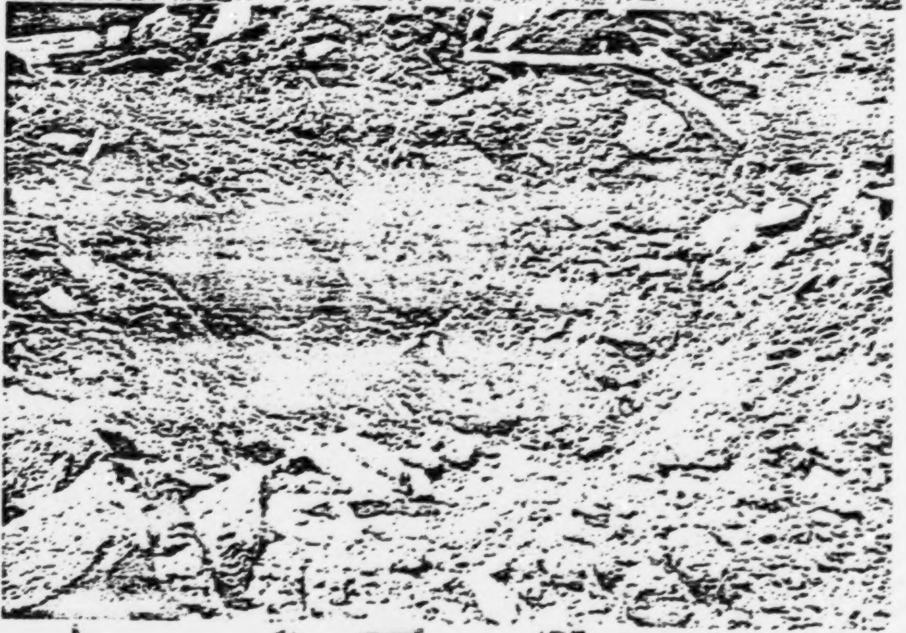
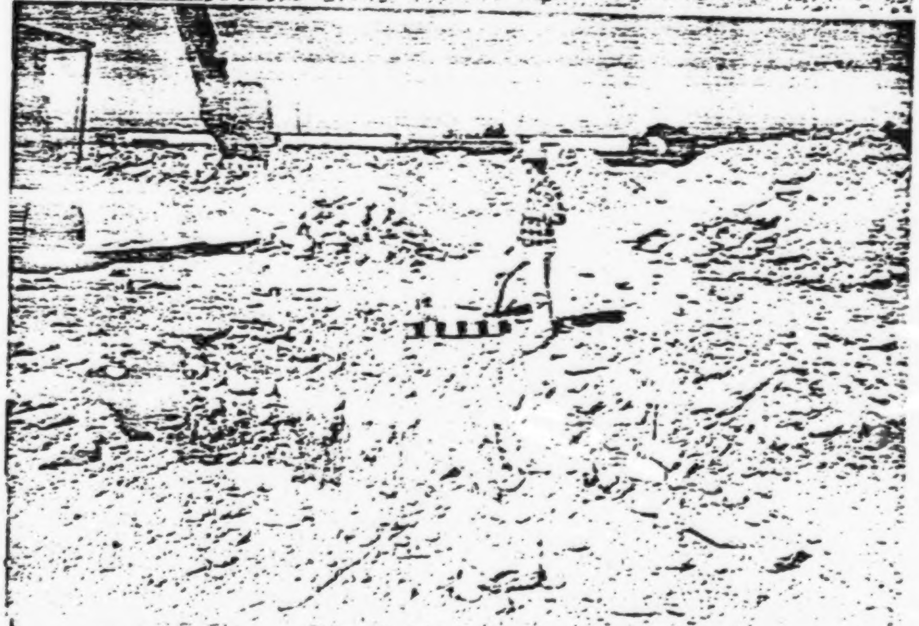


Figure 3

Photos of Crater Period 14

from Blast #3 at Allied Chemical



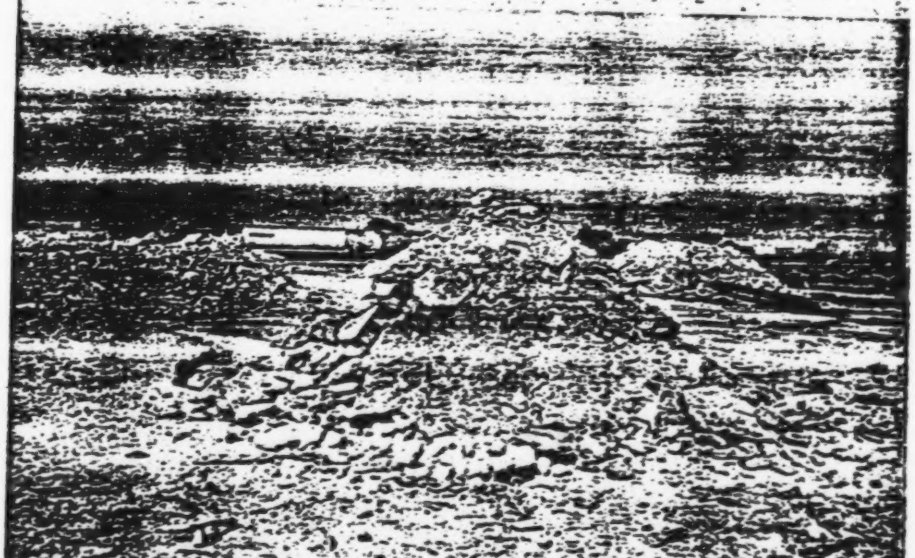


Figure 4

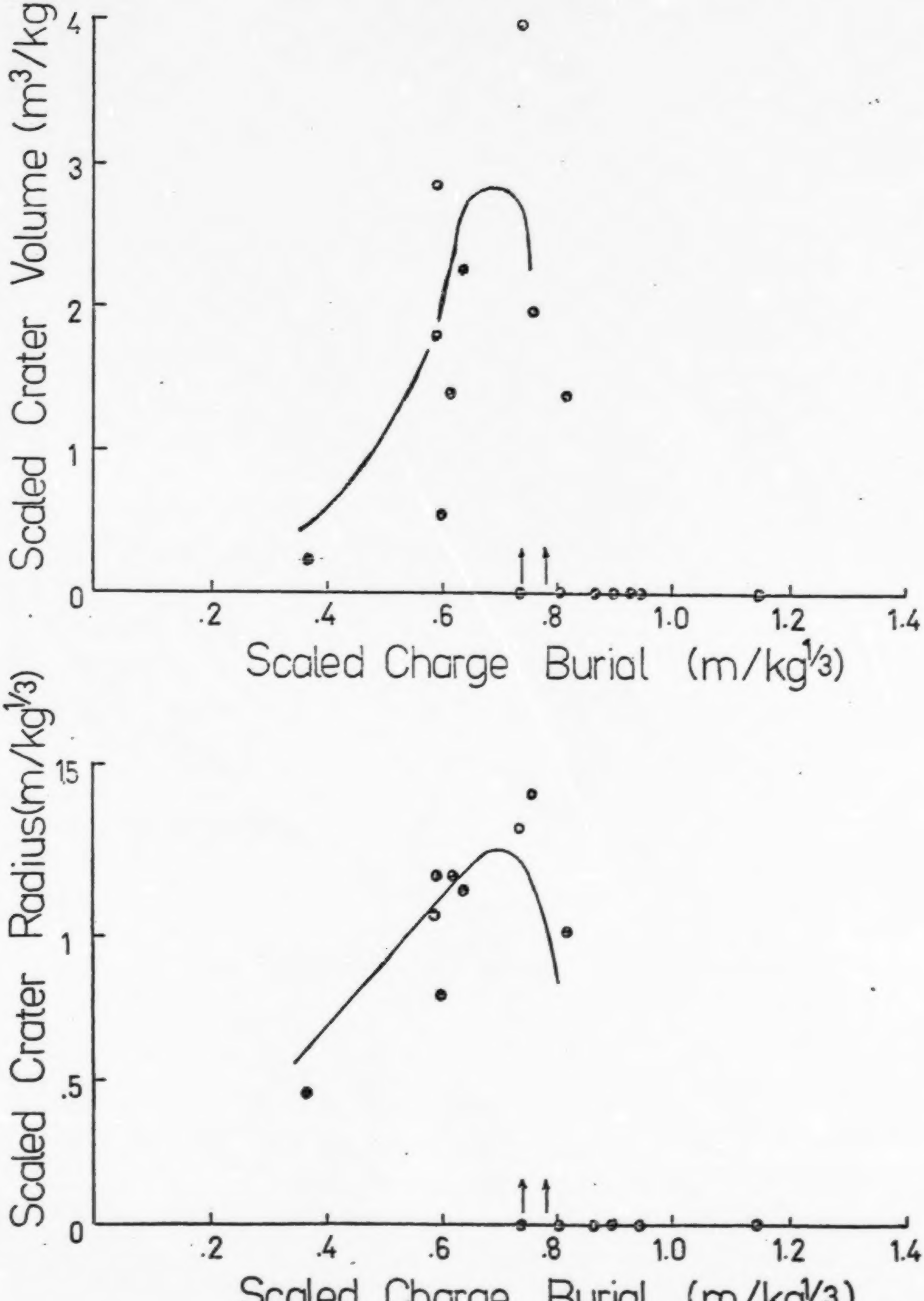

Scaled Crater Volume (m^3/kg)
4
3
2
1
0
.2
.4
.6
.8
1.0
1.2
1.4
Scaled Charge Burial (m/kg$^{1/3}$)
Scaled Crater Radius(m/kg$^{1/3}$)
1.5
1
.5
0
.2
.4
.6
.8
1.0
1.2
1.4
Scaled Charge Burial (m/kg$^{1/3}$)

Figure 5

CONTROL BLAST REFERENCE

Rating: 100 — Satisfactory Results
130 — Over-Blasted
80 — Under-Blasted

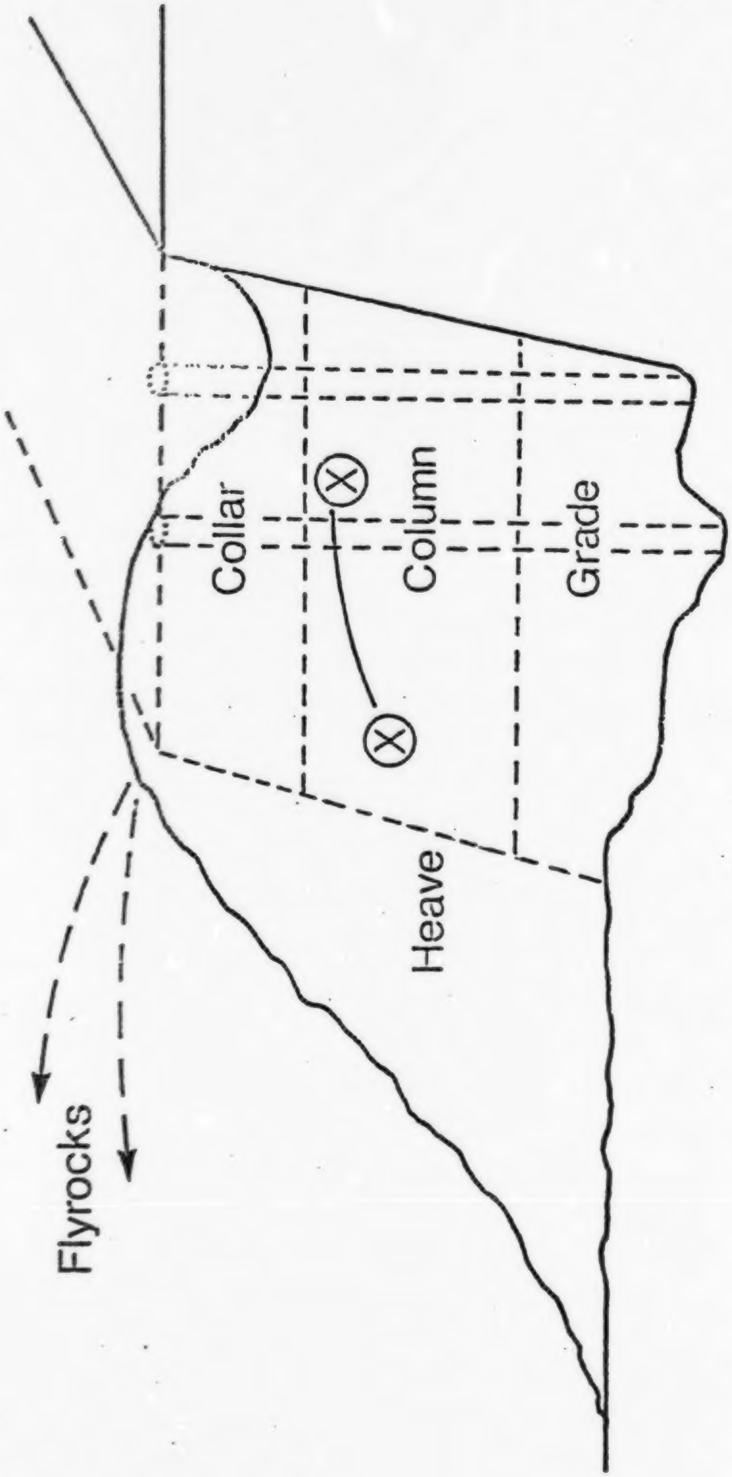
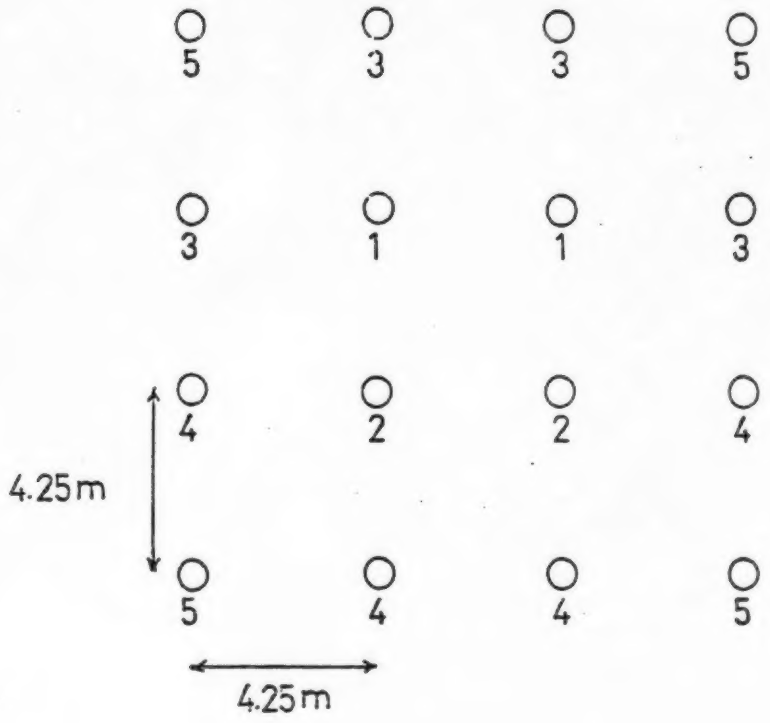

Collar
Column
Grade
Heave
Flyrocks

Figure 6


5 3 3 5
3 1 1 3
4 2 2 4
5 4 4 5
4.25m
4.25m

DELAY PATTERN

C·I·L Inc.

C·I·L House
P.O. Box 200, Station "A"
Willowdale, Ontario M2N 6H2
(416) 229-7000 Telex 06986505

July 27, 1982

bcc: G.K. Jorgenson
L. Bellamy
W. Thompson
P. Tidman

Mr. R.L. Searcy
Operations Manager
Allied Chemical Canada Limited
P.O. Box 2000
Amherstburg, Ontario
N9V 2Z6

Dear Mr. Searcy:

Re: CRATER TESTING PROCEDURES

Please find attached an outline of procedures of the crater testing, seismic monitoring and high speed filming as proposed by G. Jorgenson June 29, 1982. We understand that this test, scheduled for August 5, 1982, has been accepted by your Company.

Your support to this project is very much appreciated and we hope this study will provide useful information for establishing blasting procedures for harvesting gypsum from settling ponds.

Yours truly,

S.H. Chung
Blasting Physicist
Consulting Services
Explosives Division

SHC/lf

Attach.

C·I·L House 90 Sheppard Avenue East Willowdale, Ont.

CRATER TESTING PROCEDURES

1. Staking Drill Holes

The C-I-L technical team which includes W. Thompson, J.P. Tidman and S.H. Chung will come in the afternoon of August 4 to stake all test holes according to the attached figure.

2. Drilling and Loading

All test holes should be drilled and loaded in the morning of August 5.

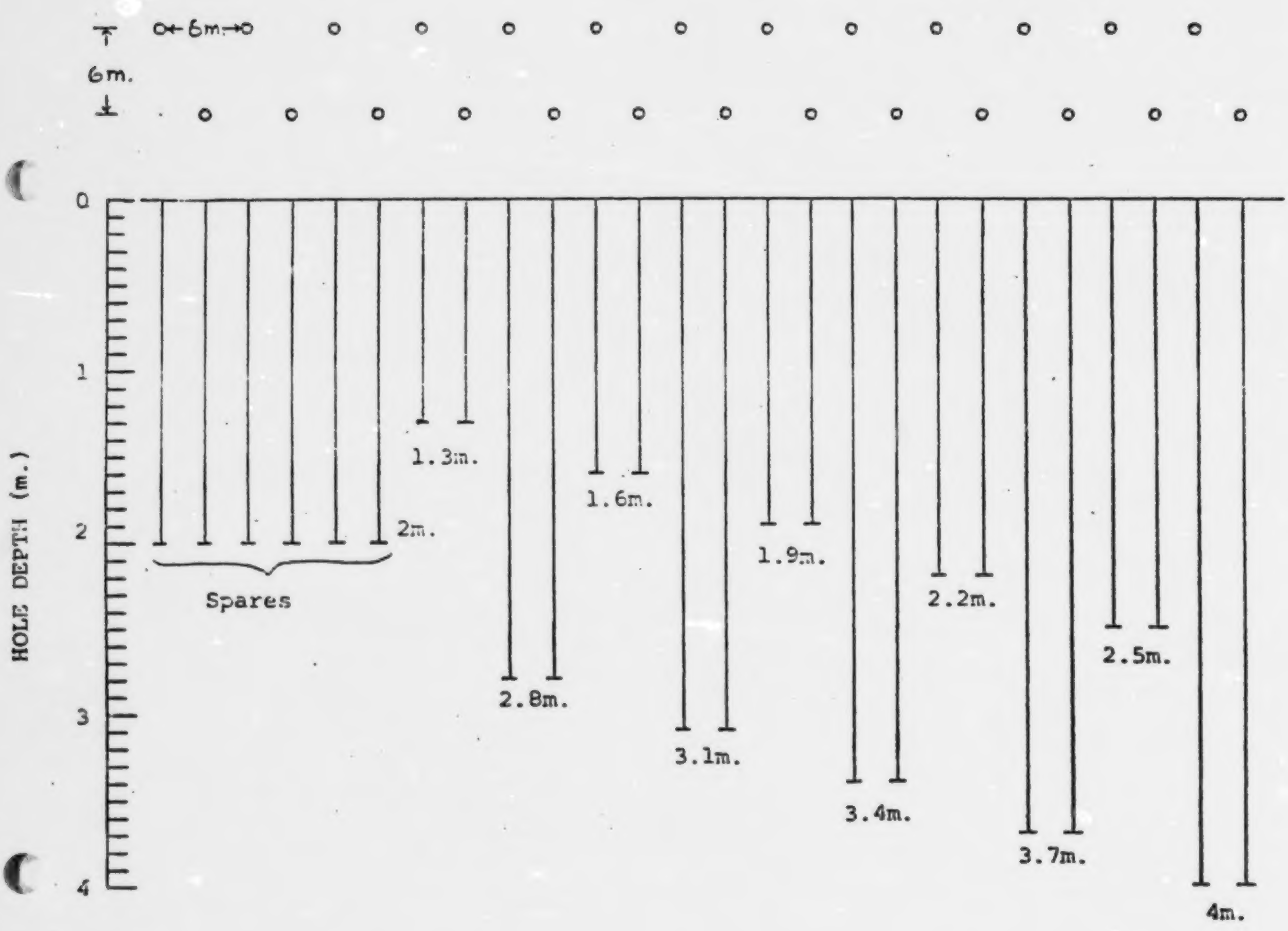
The drilling will be arranged by Allied Chemicals while the preparation of explosives and detonators will be arranged by W. Thompson, C-I-L Technical Services. The required drill hole stakes and markers for high speed filming will be provided by the C-I-L Consulting Group.

3. Firing of Shot

The C-I-L technical team will assist the blasting crew of Allied Chemicals to fire the shot. The preparation of seismic monitoring and filming will take approximately two hours, therefore the shot should be ready for firing by 3 o'clock in the afternoon.

CRATER TESTING LAYOUT

Hole Diameter : 100 mm
Explosive Type: AN/FO
Density : 0.84 gm/cc
Column Rise : 0.6 m
Weight : 4.1 kg/hole
Primer : one PROCORE Booster/hole
Initiation : Electric short period Cap
Stemming : Well stemmed drill cutting
Drill pattern : 2 rows of 12 holes


6m
6m.
HOLE DEPTH (m.)
0
1
2
3
4
2m.
Spares
1.3m.
2.8m.
1.6m.
3.1m.
1.9m.
3.4m.
2.2m.
3.7m.
2.5m.
4m.

CRATER TESTING (Continued)

	Total
AN/FO	98.4 kg
No. of PROCORE primers	24
No. of SHORT-PERIOD electric Caps -	
Periods 0,2,4,6,8 and 10 : 3 each	18
Periods 12,14,16 and 18 : 2 each	8
Duplex Connecting Wire	500 m.
Blasting Machine : 1000-Shot or CI-50	1
B-Line (Signalling for Camera)	80 m.

Shot 1 - #18 #16 #14 #12 #10 #8 #6 #4 #2 #0

Period numbers

Shot 2 - #18 #16 #14 #12 #10 #8 #6 #4 #2 #0

Shot 3 - #4 #2 #0

#8 #6

Preliminary Shot - one of the spare holes.

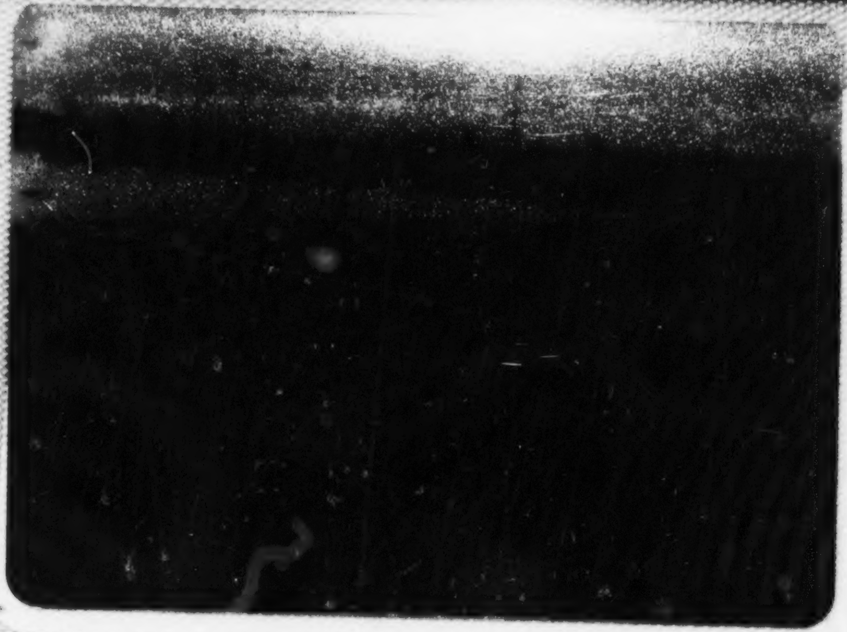
Photographs 1, 2, 3 SITE ORIENTATION

(clockwise from above)

1. HF Acid manufacturing facility of Allied Chemical at Amherstburg, Ontario

2. Gypsum disposal site (note plant in background at right).

3. Gypsum test collection pond with four parallel sites separated by internal walls.



Photographs 4, 4A, 5 **PILOT SCALE TRIAL 1.**

(clockwise from above)

4. Initial harvesting results - accomplished with a payloader. Note slabs of material due to layering upon deposit.

4A. Harvesting continued; the bed became wet due to cross-flow of residue after the trial ended.

5. Final harvest; about 700 t ready for shipment to St. Lawrence Cement.

Photographs 6, 7, 8 PILOT SCALE TRIALS 2, 3

(clockwise from above)

6. Trial 2. Pond during collection phase.

7. Trial 3. Initial use of D9-type dozer during harvesting phase.

8. Trial 3. Note considerable breakup of harvested slabs under dozer.

Photographs 9, 10 FULL SCALE POND

9. (Above) Commercial scale (18000 t) pond viewed from residue inlet point toward water level control weir. (Notch to left was used in latter tests to dewater collected coarse material).

10. (Right) Large chunks harvested with D9-type dozer from initial full scale tests. Note hard-hat for proportions.

Photographs 11, 12, 13

FULL SCALE POND

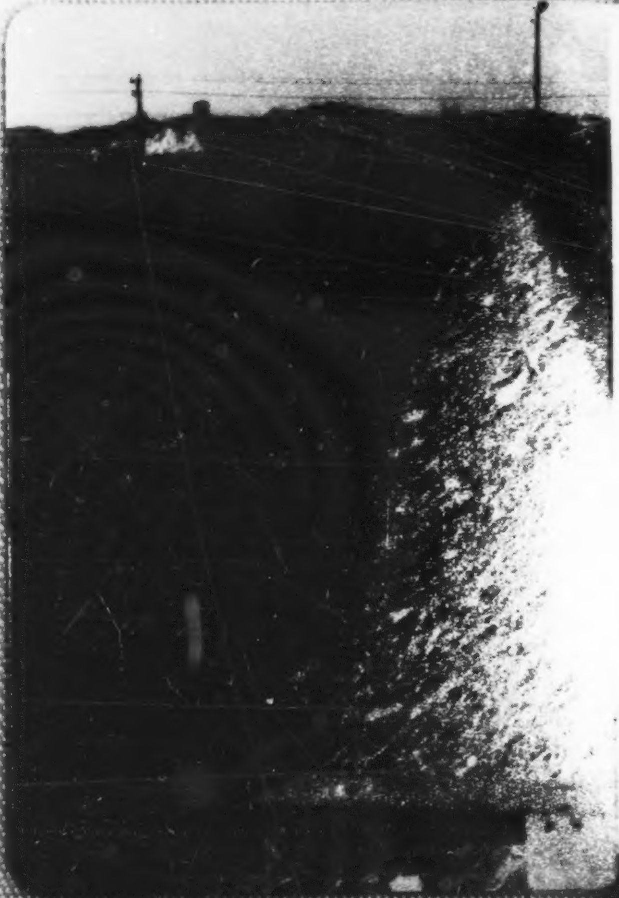
(clockwise from above)

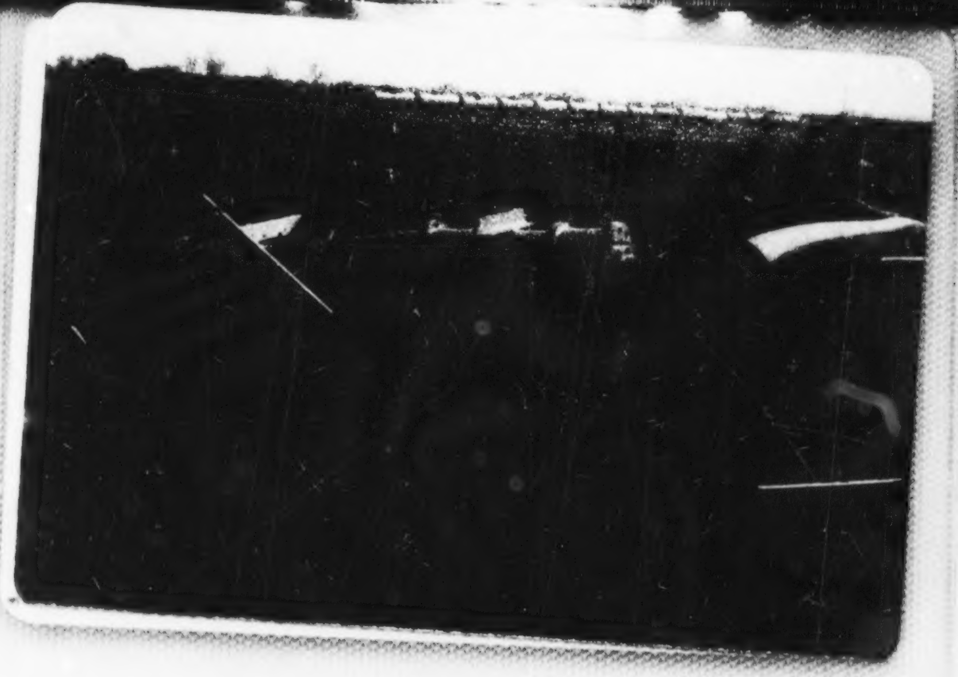
11, 12. Coarse collecting pond.

Note the hydrocyclone on the far bank used to separate the coarse from the fire material.

The near bank is open to allow dewatering of the coarse pond.

13. East half of pond where fine material (hydrocyclone overflow) was collected.





Photographs 14, 15, 16 FULL SCALE POND

(clockwise from above)

14. Note orientation of hydrocyclone. Discharge is directed toward side of coarse material collection pond. Later a flush valve was installed from the feed line to below the underflow discharge.

15. Overflow is directed toward the fine material collection pond.

16. View over hydrocyclone toward coarse pond.

Photographs 17, 18 FULL SCALE POND

17. (Above) Hydrocyclone in operation. Note thick consistency of the underflow. (Typical 40-80% solids).

18. (Right) Hydrocyclone overflow stream to fines collection pond. (Typical < 2% solids).

* Note relative flow rates.

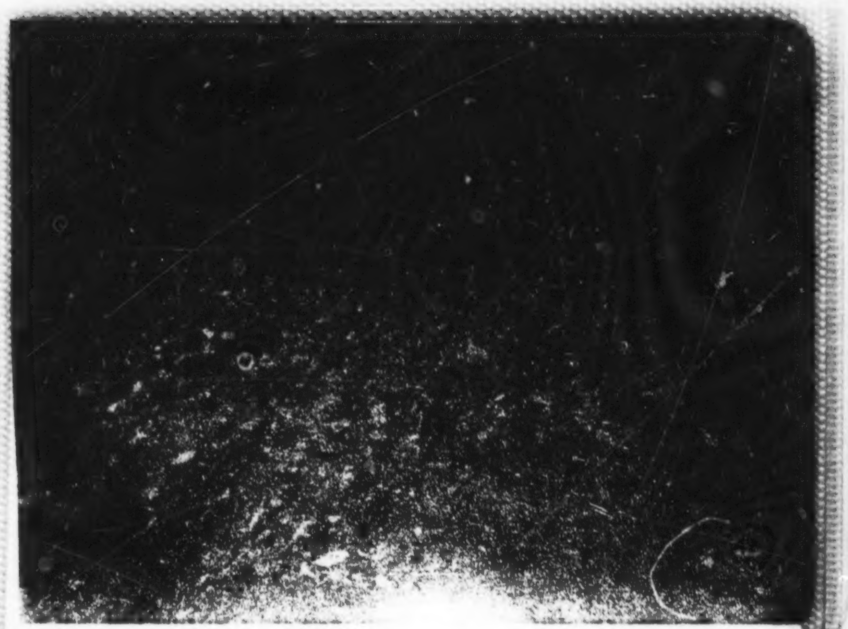
Photographs 19, 20 FULL SCALE POND

19. (Right) Core sample removed from coarse material pond.

(Scale: Pen = 13 cm).

Note particles deposited and layered texture.

20. (Below) Coarse pond during harvest with ripper bucket. Note relatively small chunks, compared to boulders removed by D9 dozer.



Photographs 21, 22 FULL SCALE POND

21. (Above) Wain - Roy bucket with frost teeth used for coarse material harvest.

22. (Right) Coarse pond during harvest with above bucket.
Material removed was transported to screening facility for product separation.

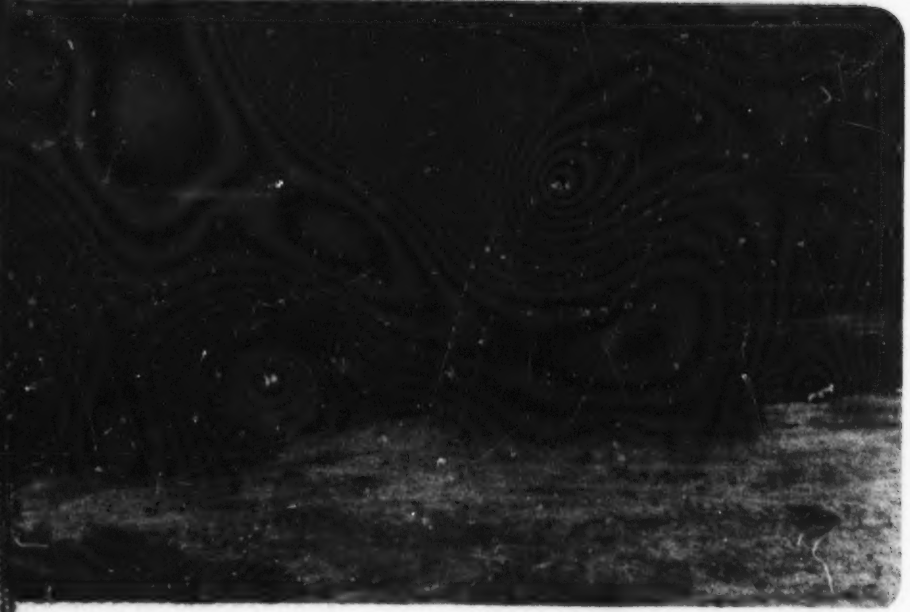
Photographs 23, 24

FULL SCALE POND

23. (Above) Close-up of chunks removed with Wain-Roy bucket. Note considerable material in product range (5-20 cm).

    (Scale: Pen = 13 cm).

24. (Right) Note layered yet cohesive mass, and marks left by Wain-Roy bucket.



Photographs **25. 26** SCREENING OPERATION

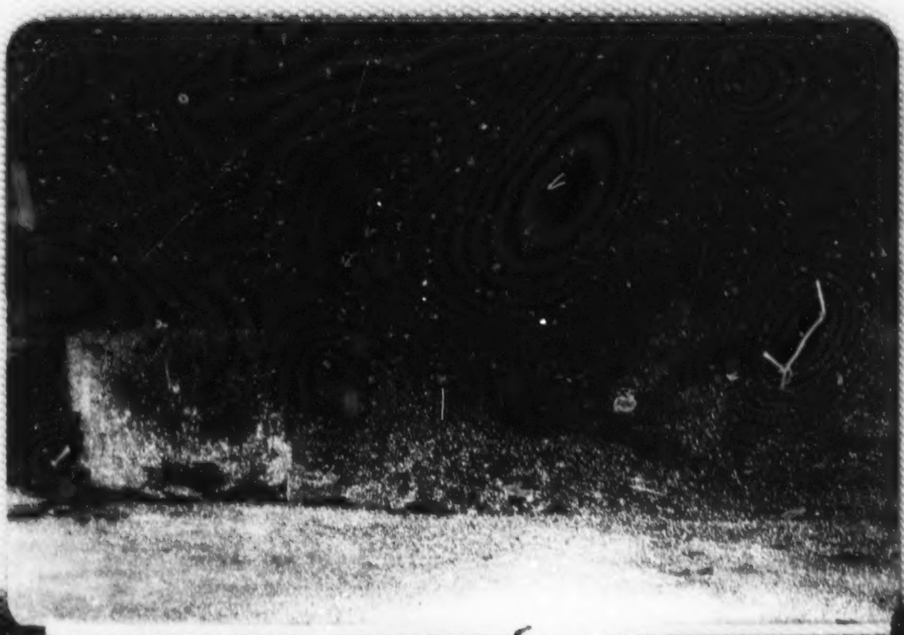
25, 26 Small scale test screen.

Note three piles in photograph above:

Left - product size 5 x 20 cm

Centre - fine rejects as sand sized gypsum

Right - oversize and small 0-5 cm rejects to
be recrushed/rescreened.

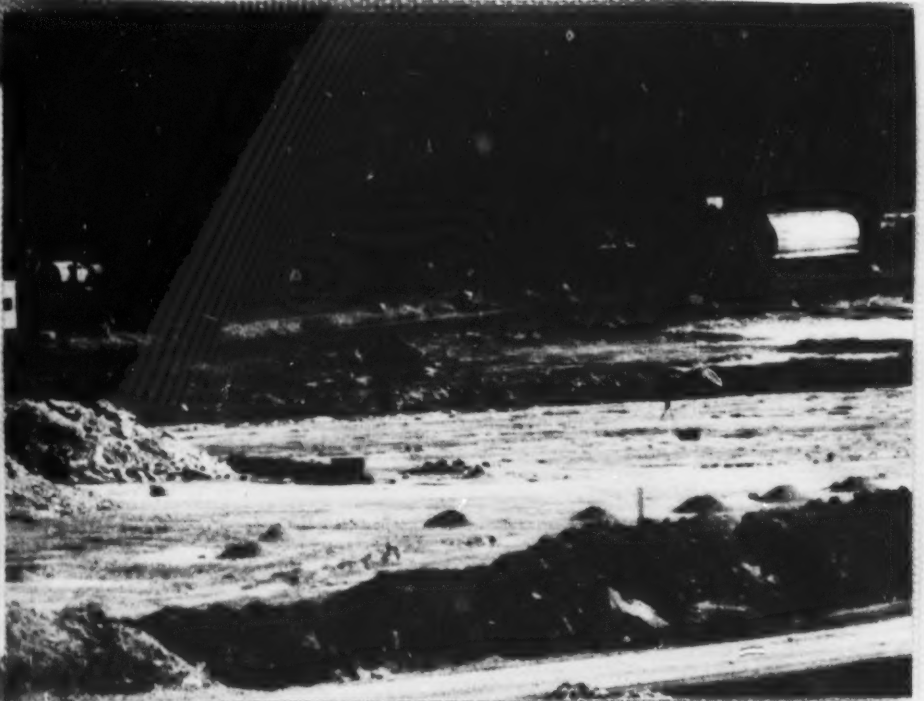


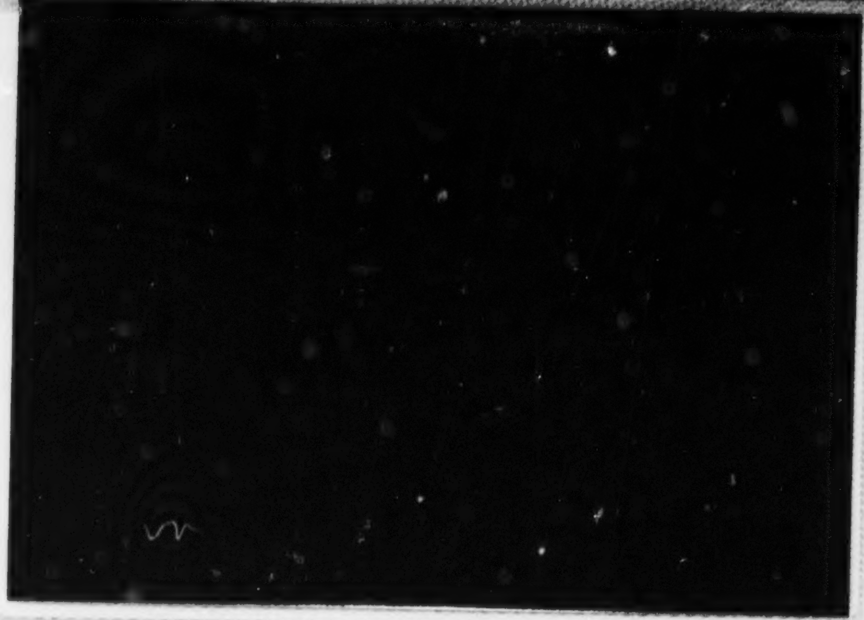
Photographs 27, 28

CIL BLAST TEST

27. (Right) Preparation of blast area on main gypsum, bed and loading of explosive into 13 holes each 10 cm dia.
1 to 2 m in depth.

28. (Below) Scene prior to sequential detonation of explosive charges.





Photographs 29, 30 **DETONATION**

Two views of the scene during sequential detonation of explosives in one-half of the test holes.

Photographs 31, 32, 33 BLAST CRATERS

(clockwise from above)

31, 32 Two views of shallow blast craters.

Note large chunks at the collar.

33. Greater depth yielded smaller pieces.

(Scale: Marker = 1 m)

Photographs 34, 35, 36 **BLAST CRATERS**

(Clockwise from above)

34, 35. Depth of 2m was achieved with deepest blast.

36. Best uniformity of size was found with deepest charge.

Subsequent screening showed a 50% product yield in the 5 x 20 cm range.

(Scale: Marker = 1 m).